

# Adjuvants for Agrichemicals

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## FOREWORD

In 1977, Dr. Cortez F. Enlowe, Jr. described agriculture in North America as the "eighth wonder of the world." Dr. Enlowe pointed out that abundant food supplies were the single most important factor in the overall advancement of the United States and Canada, giving their people the freedom to provide the central support for Western Civilization. He concluded, "the most magnificent achievement of mankind is the creation in North America of the greatest land of nutritional abundance in the world. Not even the building of the Egyptian Pyramids, the writing of the Greek Classics, the painting of the masterpieces, the composition of the symphonies, the invention of steam power, or the splitting of the atom could fill the shadow of this towering triumph of the human spirit. It alone is the greatest thing man has ever done."

This accomplishment discussed by Dr. Cortez would not have been possible without the effective use of the many highly effective agrichemicals used to control pests in modern agriculture. The importance of adjuvants to agriculture parallels that of pesticides themselves. Most herbicides and other pesticides require surfactants or other adjuvants to maximize their efficacy or utility, either in the formulated product or as an adjuvant added to the spray tank.

Agriculture is in a state of transition at a time when the world has at least 90 million new mouths to feed each year. Three of the major forces that will cause significant changes in worldwide food production are (1) the ongoing loss of land devoted to food production; (2) the increased emphasis on alternative, sustainable, or low input agriculture; and (3) the present and continuing threat of loss of registration of agrichemicals important to agriculture. Several major conservation programs were established by the U.S. Congress in the 1985 Food Security Act that include The Conservation Reserve Program, Sodbuster, Swampbuster, Conservation Compliance, and the Acreage Reduction Program. These and similar programs in other countries, especially in Europe, will result in the loss of several hundred million acres of crop land if goals are met.

Many authorities agree that increased adoption of alternative agriculture may reduce crop yields on a per unit-of-land basis. The number of registered pesticides is being reduced by state and federal regulatory actions and by private sector decisions to withdraw individual products. Public concern and regulatory complexity are likely to increase in the future causing this trend to continue. All of these forces put increased pressure on agriculture to produce an abundant food supply with fewer resources. Increased efficiency through the use of surfactants and other adjuvants will play an ever increasingly important role in maintaining our food supply.

Advances in our understanding of improved formulations, application technology, and efficient use of adjuvants to improve the efficacy of agrichemicals remains one of the major ways in which food and fiber production can be sustained with fewer agrichemicals. New complex multi-phase systems are being developed for formulations that include micro-emulsions/suspensions, multiple formulations, and other new types of emulsions. These new systems will require significant advances in the use of surfactants and other adjuvants. The use of adjuvants to improve biological activity remains poorly understood in terms of the modes of action involved. Structural activity relationships for adjuvants continue to be elusive and there is ample room for advancements in this area. One of our most urgent needs is a bioassay that can provide a predictive capability of the comparative activity of surfactants and other adjuvants with specific pesticides under field conditions. The symposium leading

to this publication and future symposia on adjuvants and agrichemicals will play an ever-increasing role in providing more effective evaluation techniques and in increasing the efficiency of adjuvants. This publication and future volumes will provide a unique resource not only for scientists in the pesticide disciplines but also for other scientists as well. The *authors and editors are commended for this major effort for making this expertise on adjuvants available for use by others.*

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## PREFACE

An estimated 50 percent or more of the world's production of food is lost to weeds, insects, diseases, and other factors. Much progress in crop protection has been made possible by the use of pesticides and other agrichemicals. Adjuvants are important to the production, marketing, application, and effective use of these chemicals. There are now over 200 pesticides registered by the U.S. Environmental Protection Agency that have specific recommendations for the use of adjuvants.

Although adjuvants have been commercially available for about 30 years, they may well be the most misunderstood crop protection products on the market today. Research is required to obtain basic information on the mode(s) of action of adjuvants and to develop practical applications of these research findings for agriculture.

The Second International Symposium on Adjuvants for Agrichemicals, held in Blacksburg, Virginia on July 31 to August 3, 1989, was designed to build upon the success of the first symposium held in 1986 in Brandon, Manitoba, Canada. Approximately 275 individuals participated in the second symposium, including 234 university faculty members and graduate students, corporate and association representatives, government regulatory officials, and private consultants. Twenty-four Asian, European, and North American countries were represented and over seventy-five scientific papers were presented.

This book, based on the second symposium, presents the topics addressed which include a bibliographic survey of research and development of agri-adjuvants; regulation and importance of adjuvants; rationale for adjuvant use; concerns within the pesticide industry relating to adjuvants; a review of the methods employed in laboratory evaluation of adjuvants; results of current research on various adjuvants (including organosilicone surfactants, oils, and emulsifiers) with herbicides, fungicides, insecticides, or growth regulators; and field, greenhouse, and laboratory methods for evaluating adjuvants. It is hoped that these topics will be of interest to many and that this book will promote a better understanding of the effects of adjuvants on pesticide penetration, translocation, photodegradation and stability, spray deposition and dissipation, and the fate of herbicides in the environment. Also, the Organizing Committees of the first and second symposia revised and updated "Formulations and Applications of Adjuvants for Agrichemicals: A Selected Bibliography of World Literature in English" for use by agricultural researchers and others.

Chester L. Foy

## THE EDITOR

Dr. Chester L. Foy is now Professor of Plant Physiology and Weed Science at Virginia Polytechnic Institute and State University, Blacksburg. He received the B.S. degree from the University of Tennessee, M.S. degree from the University of Missouri, and Ph.D. from the University of California-Davis. He joined Virginia Polytechnic Institute as Associate Professor in 1966, was promoted to Professor 1968, and served (1974 to 1980) as Head of the Department now known as Plant Pathology, Physiology, and Weed Science. Formerly he was at the University of California-Davis as Associate Botanist and Associate Professor of Agricultural Botany (1964 to 1966), Assistant Botanist (1958 to 1964), and Graduate Assistant (1953 to 1956). Earlier he was Assistant Instructor (Field Crops) at the University of Missouri (1952 to 1953).

Dr. Foy is a charter member of the Weed Science Society of America (WSSA) and the International Weed Science Society (IWSS). He is currently (1991-93) serving as President of IWSS and has served as President of WSSA. His affiliations with other professional organizations past and present include American Society of Agronomy, American Association for the Advancement of Science, American Institute of Biological Sciences, American Society of Plant Physiologists, Council of Agricultural Science and Technology, International Congress of Plant Protection, International Congress of Pesticide Chemistry, Plant Growth Regulator Society of America, Southern Weed Science Society (SWSS), Torch International, and Virginia Academy of Sciences. Dr. Foy's recognitions include election to membership in several academic honorary societies, and several "Who's Who" listings. Other awards for professional achievement include National Academy of Sciences Resident Research Associate Award, Gamma Sigma Delta Faculty Research Award, WSSA Outstanding Paper Award, WSSA Fellow, SWSS's first "Weed Scientist of the Year" Award, and WSSA's "Outstanding Researcher" Award.

Dr. Foy served as Editor of *Reviews of Weed Science* and is currently serving as Editor of *Weed Technology*. He is a charter (and current) member of the editorial board of the international journal, *Pesticide Biochemistry and Physiology*, and has served many years as WSSA Associate Editor and Reviewer for *Weed Science*, as well as Reviewer for several other scientific journals.

Dr. Foy conducts and directs field, greenhouse, and laboratory studies in the following areas: crop production and protection; vegetation management in agronomic and fruit crops, and control of specific perennial weeds; routes and mechanisms of absorption, translocation, accumulation, and exudation of herbicides and growth regulators, surfactants, and other adjuvants; metabolism and fate of these substances; physiological, biochemical, and morphological changes induced by exogenous chemicals; modes of action and selectivity of herbicides and growth regulators; minimizing pesticide residues in the biosphere; allelopathy; and parasitic weeds. His publications include 21 book chapters; 5 book reviews; more than 90 peer-reviewed scientific journal papers; 5 technical research bulletins; over 340 contributions to conference proceedings, research reports, abstracts or scientific papers, and special technical research articles; and more than 200 semi-technical or extension publications.

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## ADJUVANTS AND AGROCHEMICALS\*

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## *Section I*

A Bibliographic Survey; Physiological Action; Effects on Pesticide  
Penetration, Translocation, Photodegradation, and Stability

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## Chapter 1

# RESEARCH AND DEVELOPMENT OF AGRO-ADJUVANTS: A BIBLIOGRAPHIC SURVEY

Paul N. P. Chow and Cynthia A. Grant

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## ABSTRACT

This bibliographic survey reflects the research and development of agro-adjuvants in the past and today. In view of concerns on economic stress and chemical residues in the environment, future research and development of agro-adjuvants should emphasize renewable, biodegradable, and inexpensive raw materials such as crop oils and carbohydrates. New adjuvants should be more efficient, nontoxic, have less impact on the environment, and maximize the activity of pesticides. However, research efforts should not ignore an investigation of the metabolism and mode-of-action of adjuvants per se, their physiological effects on plants, and their role in pesticide formulation and application.

## I. INTRODUCTION

Recognized pesticides have contributed greatly to the reduction of crop losses, resulting in increased crop yields and lower crop production costs. It is estimated that farmers in western Canada used 17.5 million kilograms of herbicides to control weed pests in 1985, and American farmers applied 182 million kilograms of herbicides and spent \$3.6 billion for chemical weed control in 1976. All herbicides require adjuvants to maximize the efficiency of their herbicidal activity, thereby reducing the rate of active ingredients entering the environment. Close cooperation among industry, universities, and government research organizations have, needless to say, contributed greatly to the successful development of pesticides, adjuvants, and other agrochemicals.

A vast amount of literature on agro-adjuvants and pesticides has been published every year in international scientific journals, monographs, and proceedings. The first edition of the adjuvant bibliography was compiled and published as a compendium of the literature up to 1986.<sup>3</sup> The second edition was expanded, revised, and issued as an appendix in *Adjuvants and Agrochemicals* by CRC Press in March, 1989.<sup>10</sup> Since 1986, a literature search of adjuvant formulations and their new application techniques was edited as another adjuvant bibliography.<sup>5</sup> A total of three searches in adjuvant literature located approximately 2000 references.

A survey of the bibliography of adjuvant literature over 60 years (1926 to 1989) revealed some interesting results, which will be discussed in this article.

## II. BIBLIOGRAPHIC SURVEY

### A. NUMBER OF PUBLICATIONS

In the early 1920s to 1940s, only one or two articles on the application of agro-adjuvants were published each year (Figure 1). As time progressed, the number of publications on adjuvants or related articles in various international journals increased at a rapid pace. In the 1960s, 90 to 150 articles were published during each 5-year period. During the 1970s and 1980s, more than 230 and 360 articles appeared in a 5-year interval, respectively. The number of publications continues to increase, as indicated by the 85 articles published in 1986.

It appears that the investigation of adjuvants has received more attention in the last 20 years. This can be seen in the comparison of 1966 and 1986, for example (Figure 1). There were more than three times as many publications in 1981 to 1986 than in 1961 to 1966. The reason may be associated with development of contact pesticides derived from cheap raw materials. In the early 1900s and 1920s, inorganic salts were used for controlling weeds, and kerosene and soap solutions were used for killing insects. Applied at high rates, these nonselective products did not need the aid of adjuvants to maximize their killing actions.

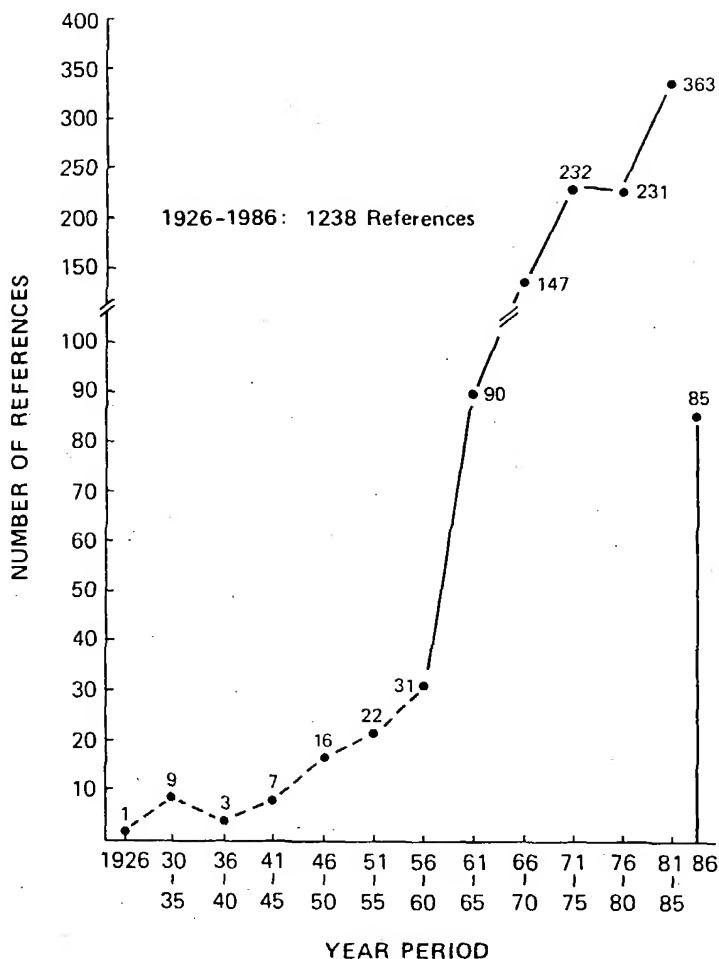


FIGURE 1. Number of publications of agro-adjuvants during the period of 1926 to 1986.

Although adjuvants had "wonderful", "magic" effects on the activity of herbicides,<sup>4,6</sup> the cost of applied herbicides in crop production was relatively low. Greater than recommended rates were applied to ensure better pest control. The sale of excess pesticides could also economically benefit the industry and encourage the development of more products. However, during the last 15 years, the economics of petroleum-based materials has changed rapidly and their components are no longer cheap. Therefore, research scientists and the chemical industry turned their efforts toward developing more efficient and cheaper adjuvants as well as pesticides. The efforts were fruitful. For example, the widespread use of a diuron mixture (Karmex) in the United States and the successful application of diclofop-methyl (Hoe-Grass, Hoelon) and sethoxydim (Poast, BAS 9152) mixed with adjuvants for weed control in Canada promoted a rapid increase in the use of adjuvants. European investigations have also demonstrated that the addition of appropriate adjuvants in the spray solution, prior to application, allowed a substantial reduction of the rates of pesticide ingredients required for effective pest control.<sup>1</sup> Thus, a number of adjuvant companies and dealers in Europe and North America have been established, and the sale of adjuvants has increased in recent years.

## B. CLASSIFICATION OF BIBLIOGRAPHY

A total of 1490 references (from 1926 to May 1989) were derived into nine categories (Figure 2) based on their titles. It is interesting to note that over 70% of the articles dealt with physicochemistry and application techniques, from atomization and deposition size of formulations to agronomic aspects. Therefore, adjuvant effects on modifying the physical and chemical properties of the pesticide spray solutions are well documented. It is surprising that very few articles evaluated the "economic" impact of adjuvants added to herbicides or the impact on the "environment". Two cases may be worth mentioning here. Diclofop-methyl was initially registered at 1.1 kg/ha in Canada. Further testing including adjuvants met with success and the rate was reduced to 0.8 kg/ha and then to 0.6 kg/ha, with equal effectiveness in controlling grass weeds. Use of the reduced rate also increased the tolerance of barley to the herbicide.<sup>2</sup> A number of articles in the application category were found which investigated crop oil-based adjuvants with new grass killers, due to the economic advantage of their low application cost.

Adjuvants play an important role by inducing physiological responses directly or indirectly associated with phytotoxicity. For example, ethylene synthesis and phytotoxicity induced by agrichemicals (growth regulators, herbicides, surfactants, etc.) has been investigated in comparative detail.<sup>7</sup> However, as shown in Figure 2, metabolic study on surfactants in plants is limited.<sup>8,9</sup> Only one article related to the mode of action and physiological effect of oils on plant tissues was found, in which the author proposed that stomata penetration of oils was the principal path of entrance of oil into leaves.<sup>11</sup>

## III. APPENDIX — SELECTED RELEVANT BIBLIOGRAPHY

The large number of entries in the bibliography of agro-adjuvants (about 2000 references in three sources) makes searching for needed references difficult and time consuming. Therefore, a selected relevant bibliography with 180 references in 7 classes and 21 subclasses as an appendix may provide a useful guide for finding references for research needs within a short time period.

The selection of references for a given category is intended to be a representative list from which readers may find more references in the reference section of each article. If an author published more than one article with a similar subject, only the most recent one was entered. Omission of the other articles does not indicate any bias in selection, nor does inclusion imply the best selection, as it is impossible to evaluate the content of each article within a limited time.

### A. GENERAL

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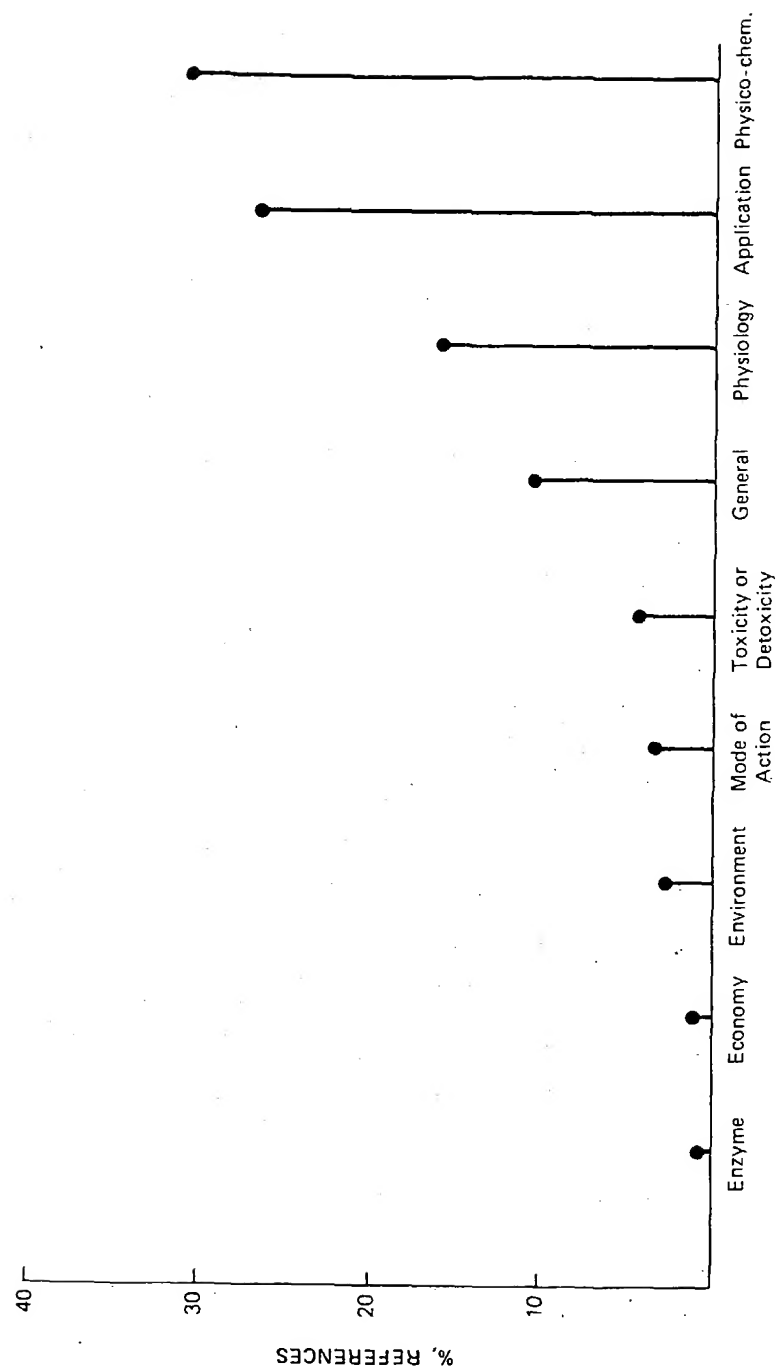


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## Chapter 2

**ANALYSIS OF EFFECTS OF SURFACTANTS ON  
PERMEABILITY OF PLANT CUTICLES**

Jörg Schönherr and Hubert Bauer

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## ABSTRACT

The effects of surfactants on solute (2,4-D) and the water permeability of isolated cuticular membranes (CMs) were measured. In analyzing the data, surfactant effects on partition coefficients (K) and on diffusion coefficients in cuticles (D) are distinguished. Surfactants in donor solutions at concentrations above the critical micelle concentration (cmc) slow the penetration of solutes which are soluble in surfactant micelles. This effect is due to the reduced partition coefficients (cuticle/water) of solutes when the water contains surfactant micelles, and is called K-depression. Surfactants may also increase the mobility (D) of solute and water molecules in cuticles. This effect was studied using unilateral desorption of solutes from the outer surface (UDOS). In these experiments, 2,4-D sorbed in CMs must diffuse through a thin layer located at the outer surface of the CM. This skin of the CM is the layer that limits the velocity of desorption of 2,4-D. Rate constants of desorption using an inert phospholipid suspension and micellar surfactant solutions are compared. With surfactant solutions, rate constants of desorption were larger by a factor of up to about 40. Surfactant effects on rate constants of desorption increased with time and depended on the initial permeability of the CMs. This effect of surfactants is due to an increased mobility of 2,4-D in the limiting skin of the CM and requires the presence of surfactants in the CM. Our data and analysis show that activator surfactants must overcompensate K-depression by increasing diffusion coefficients in the limiting skin of the CM. Since activator surfactants must penetrate into cuticles, their effects depend on external concentrations, cuticle/water partition coefficients, and the diffusion coefficients of the surfactants. It is argued that activation of solute diffusion in CMs is due to increased segmental chain mobility in cutin and amorphous regions of soluble cuticular lipids (wax). Since water and solute permeation across cuticles are limited by the same barrier, the effects of surfactants on water and solute permeability are similar. Both the transpiration test and UDOS are suitable for screening surfactants and formulations for the activation of cuticular penetration of solutes.

## I. INTRODUCTION

Surfactants are important constituents of pesticidal formulations. In conjunction with other adjuvants, they may function as spreaders, stickers, antifoamers, compatibility agents, or activators.<sup>11</sup> Activator adjuvants improve the efficacy of a formulation. It has been suggested that they function primarily by altering solubility relationships and therefore affect the ability of a pesticide to penetrate the cuticle.<sup>24</sup> This hypothesis puts the site of action of surfactants on the surface of the cuticle, and penetration of cuticles by surfactants would not be required for activation. In the meantime, it has been demonstrated that surfactants can penetrate cuticles rapidly and in substantial quantities.<sup>22</sup> Convincing evidence has been presented showing that surfactants penetrate the cuticles together with the active ingredients and that this copenetration might be one prerequisite for activation of the penetration of active ingredients.<sup>7,10,22</sup>

While it is well established that surfactants can speed up the penetration of active ingredients and water,<sup>4,16</sup> their mode of action at the level of the cuticle is not at all clear.<sup>7</sup> Diffusion across the cuticle is the rate-limiting step in foliar penetration from solutions.<sup>19</sup> If penetration occurs from more or less dry residues that remain on the cuticle after water and other volatile constituents of spray liquids have evaporated, the transition of active ingredients from the residue into the cuticle may add to the total resistance of the diffusive pathway. In addition to affecting coverage, retention, and the physical state of the residue on the surface of the cuticle, an activator surfactant could enhance penetration by changing



the structure and composition of cuticles. This could increase the diffusion coefficients in cuticles and therefore speed up penetration.

The complexity of solute uptake is one reason why the structure-activity relationships for surfactants in foliar penetration have remained obscure so far. Furthermore, in classical field and droplet experiments, many factors affecting uptake act and interact simultaneously. The contributions of individual factors to biological activity or to the amounts of active ingredients that have penetrated in a certain time cannot be separated. To overcome these difficulties, we have developed two test systems that specifically measure the mobility of water and solutes in plant cuticles. All other factors involved in foliar penetration from droplets and residues are absent in these tests.

## II. MATERIALS AND METHODS

### A. CUTICULAR MEMBRANES

Astomatous cuticles isolated enzymatically from mature green fruits of pepper (*Capsicum annuum* L. cv. Bell Boy), ripe fruits of egg plant (*Solanum melongena* L. cv. Black King), and the upper surfaces of mature leaves of bitter orange trees (*Citrus aurantium* L.) and pear trees (*Pyrus communis* L., cv. Bartlett) were used in the tests.<sup>17</sup> Isolated cuticles will be referred to as cuticular membranes (CMs). CMs from which waxes were extracted in a Soxhlet apparatus using chloroform will be referred to as polymer matrix membranes (MX membranes).

Fruits and leaves were taken from plants grown under controlled conditions in walk-in growth chambers (for details see Reference 5). Plants grew vigorously, remained healthy, and it was not necessary to use pesticides. The cuticles had therefore never been exposed to surfactants or pesticides prior to experimentation.

### B. CHEMICALS

Diffusion across CMs and MX membranes was followed using radiolabeled solutes. (2,4-Dichlorophenoxy)-[2-<sup>14</sup>C]acetic acid (2,4-D; specific activity 2.04 GBq/mmol) was obtained from Amersham Buchler (Braunschweig, Germany). Polydisperse [phenyl-<sup>3</sup>H(N)]-Triton X-100 (specific activity 166.5 GBq/mg) was purchased from NEN (Dreieich, Germany). All other nonlabeled surfactants (Table 1) were polydisperse, with the exception of SDS, and were applied as unbuffered aqueous solutions unless stated otherwise. 2,4-D was dissolved in 0.01 M potassium citrate buffer adjusted to pH 2.0.

A 1% (w/v) phospholipid suspension (soybean lecithin; Serva, Heidelberg, Germany) was used as a medium in the desorption studies. It was prepared by sonicating water and lecithin at 60°C for 15 min at full power using a Branson B-12 sonifier. NaN<sub>3</sub> (1 mmol) was added to the suspension to prevent the growth of microorganisms during the course of the desorption studies. This mixture was stable for months and will be referred to as phospholipid suspension (PLS).

Emulsions were prepared using low-viscosity paraffin oil (Merck 7174, Darmstadt, FRG) and the nonionic surfactants Brij 30, Brij 56, Myrj 45, and Tween 85. Paraffin oil (1.4 g) and surfactant (0.6 g) were mixed and diluted with water, resulting in a nominal coverage of 2 mg/cm<sup>2</sup> on the surfaces of the CMs.

### C. PROCEDURES

The effect of surfactants on the water permeability of bitter orange and pear leaf CMs was studied using the transpiration test of Geyer and Schönherr.<sup>4</sup> Each CM was mounted on top of a transpiration chamber filled with water. The chambers were stored over dry silica gel (25 ± 1°C) and weighed repeatedly to monitor water loss through the CMs. When

TABLE 1  
Surfactants Used for Experimentation

Trade name	Chemical name	nEO <sup>a</sup>	HLB <sup>b</sup>	Source <sup>c</sup>
SDS	Sodium dodecylsulfate	—	40.0	1
Triton X-100	<i>p</i> -( <i>t</i> -Octylphenyl)- $\omega$ -hydroxypoly(oxy-1,2-ethanediyl)	10	13.5	1
Triton X-35	<i>p</i> -( <i>t</i> -Octylphenyl)- $\omega$ -hydroxypoly(oxy-1,2-ethanediyl)	3	7.8	1
Brij 30	Dodecyl- $\omega$ -hydroxypoly(oxy-1,2-ethanediyl)	3	9.8	2
Brij 56	Hexadecyl- $\omega$ -hydroxypoly(oxy-1,2-ethanediyl)	9	12.9	2
Myrj 45	Polyoxyethylene stearic acid (monoester)	8	11.1	2
Tween 85	Polyoxyethylene sorbitol trioleate	20	11.0	1
Renex 36	Tridecyl- $\omega$ -hydroxypoly(oxy-1,2-ethanediyl)	6	11.6	2
Ethomeen C12	Bis(2-hydroxyethyl)cocoamine	1	10.2	3
Ethomeen C15	Polyoxyethylene cocoamine	5	17.9	3
Ethomeen T15	Polyoxyethylene tallowamine	5	14.9	3
Ethomeen T25	Polyoxyethylene tallowamine	15	19.3	3
Ethomeen S15	Polyoxyethylene oleylamine	5	14.6	3
Ethomeen S25	Polyoxyethylene oleylamine	15	19.2	3
Ethomeen HT15	Polyoxyethylene stearylamine	5	15.0	3
Ethomeen HT25	Polyoxyethylene stearylamine	15	—	3
Ethomeen HT60	Polyoxyethylene stearylamine	50	19.7	3

Note: SDS was reagent grade; all other surfactants were polydisperse and technical grade.

<sup>a</sup> Weighted mean of ethoxy groups per molecule of polydisperse surfactant.

<sup>b</sup> The hydrophile-lipophile balance (HLB) figures were taken from References 1, 6, 12, or from data sheets of the manufacturer.

<sup>c</sup> 1 = Serva, Heidelberg, Germany; 2 = Atlas Chemie, Essen, Germany; 3 = Akzo Chemie, Duren, Germany.

the water permeability of each CM had been established with good accuracy, aqueous surfactant solutions (50  $\mu$ l) were applied to the morphological outer surface of the CM, resulting in a nominal coverage of 2 mg/cm<sup>2</sup>. The effective coverage is only about half that amount, due to deposition of the surfactant on the apparatus.<sup>4</sup> When the water from the treating solutions had evaporated, weighing of the chambers was resumed as before. The ratio of the weight vs. time slopes after and prior to treatment with surfactant is a measure of the effectiveness of a surfactant. This ratio was calculated for each CM separately (paired observations). If a surfactant has no effect on water permeability, the ratio will be unity. The ratio will be larger than 1 if the surfactant increases water permeability. Deviations from unity were significant at the 95% level when the ratios were smaller than 0.7 or larger than 1.3. Means were calculated from effects observed for individual membranes. Standard deviations mainly represent variations in surfactant effects among CMs.

Water permeance (P) is the flow of water per unit area and driving force (liquid state), and was calculated using Equation 1:

$$P = (\Delta M / \Delta t) / (A \times \Delta C) \quad (1)$$

where the numerator represents the steady-state flow of water from the chambers (in kilograms per second), A is the surface area of the membrane exposed to water and silica gel (1.13  $\times 10^{-4}$  m<sup>2</sup>), and  $\Delta C$  is the driving force for which 1000 kg/m<sup>3</sup> were used, as the water concentration over dry silica gel is practically zero.

The effect of surfactants on solute permeability was studied using two different methods. Surfactant effects on the permeability of MX membranes was measured using the method of Kerler et al.<sup>8</sup> The MX membranes were inserted between the donor and receiver chambers

of the transport apparatus. The donor solutions containing radiolabeled 2,4-D and nonlabeled surfactant buffered at pH 2.0 faced the morphological inner surface of the membranes. A PLS served as receiver on the outer surface of the MX membranes. The apparatus was thermostated at  $25 \pm 1^\circ\text{C}$ , and both donor and receiver solutions were stirred vigorously. The amount of 2,4-D that diffused across the membranes was measured as a function of time and, from the steady-state slope of a plot amount (M in dpm) diffused vs. time (t in s), the permeance (P) was calculated according to Equation 1, where A is the membrane area exposed to the solutions ( $0.38 \times 10^{-4} \text{ m}^2$ ) and  $\Delta C$  is the concentration gradient (dpm per cubic meter) of nondissociated 2,4-D calculated from the  $\text{pK}_a$  (2.73) and the pH (2.0) of the donor. The concentration gradient across the membranes is solely determined by the concentration of the donor, as the 2,4-D concentration in the water is essentially zero in the receiver because the lipophilic 2,4-D is sorbed preferentially in the phospholipid aggregates of the PLS. This keeps the concentration of 2,4-D in water practically zero. In some early experiments, a 0.01 M borax buffer (pH 9.1) was used as receiver. At this pH, all 2,4-D in the receiver is ionized and the concentration of nonionized 2,4-D is also zero. By using the method of paired observations, the effectiveness of borax buffer and PLS as receiver media was compared and found to be identical (data not shown).

The donor concentration of 2,4-D was determined from aliquots of the donor solutions after the steady state had been reached. The amount of 2,4-D sorbed in the MX membranes was determined by carefully cutting out the areas of the membranes exposed to the solutions at the end of the experiments. They were blotted lightly to remove adhering solutions, and radioactivity was determined by scintillation counting (see below). The partition coefficient ( $K_{\text{mx/w}}$ ) for the MX/water system was calculated from the mass of the MX (in kilograms), the radioactivity (in dpm) in the MX, and the equilibrium concentration of nonionized 2,4-D in the donor solution (dpm per kilogram) according to Equation 2:

$$K_{\text{mx/w}} = C_{\text{mx}}/C_{\text{donor}} \quad (2)$$

The permeance (P) as defined in Equation 1 is based on the concentration of nonionized 2,4-D in the donor solution. Since in these experiments the concentration of 2,4-D in the MX membranes was known, an alternative permeance denoted  $P^*$  could be calculated using the concentration of 2,4-D in the MX membranes rather than the concentration of the donor solution. It follows from the definition of the partition coefficient (Equation 2) that the relationship between P and  $P^*$  is simply

$$P^* = P/K_{\text{mx/w}} \quad (3)$$

$P^*$  is independent of the partition coefficient and therefore a measure of mobility (see below).

UDOS was used to study the effects of surfactants on the solute permeability of the CMs. The CMs were mounted between the sorption and desorption compartments of the apparatus shown in Figure 1. The desorption compartments were manufactured from conventional stainless steel (V2A) and the sorption compartments from Novorox FALC 22 3 (Krupp Südwestfalen AG, Siegen, Germany). This ferritic/austenitic steel is needed when solutions having a pH  $< 3$  are to be used in the sorption compartments. The contact areas of the sorption and desorption compartments were greased lightly (Hochvakuum silikonfett, Wacker Chemie, München, Germany) to ensure a good seal. They were held together by three screws, with the CMs sandwiched in between. The inner surface of the CMs faced the sorption compartment.

The CMs were loaded with radiolabeled 2,4-D by adding a buffered solution (200  $\mu\text{l}$ , pH 2.0) to the sorption compartment, which was left open so that the water could evaporate.

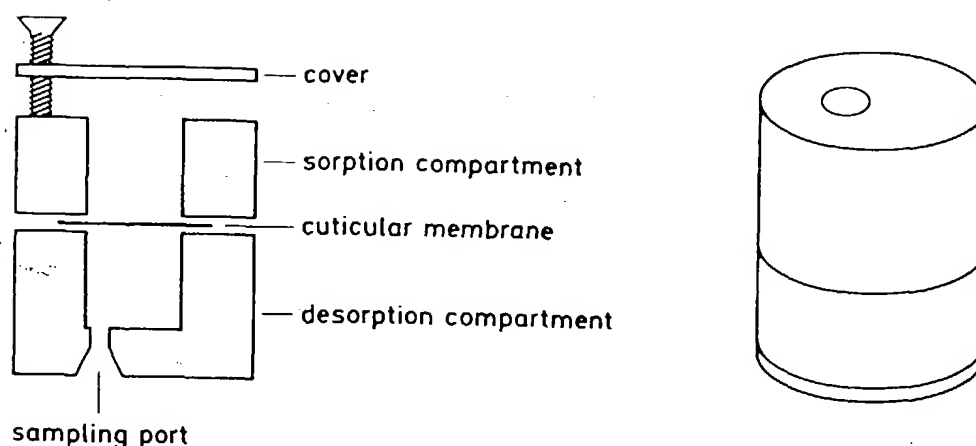


FIGURE 1. Apparatus used for unilateral desorption from the outer surface (UDOS).

If the evaporation of water is sufficiently slow, all 2,4-D will be sorbed in the CMs, and no residue will remain on the surface of the cuticle when all the water has evaporated. When the chambers were left standing without agitation on the top of the bench at ambient temperatures, sorption of 2,4-D in cuticles proceeded faster than evaporation of water. This was checked using  $^{14}\text{C}$ -labeled 2,4-D and tritiated water. The  $^3\text{H}/^{14}\text{C}$  ratio increased from 4 to 10 within 1 h and stayed at about that value until the water had evaporated after about 6 h (data not shown). As an alternative, loading can be performed with the sorption chambers covered. In this case, sorption solutions were removed after equilibrium had been established (24 h). This procedure was equally acceptable (data not shown), but large amounts of radiolabeled 2,4-D are wasted when the sorption solutions are discarded after equilibration.

It should be pointed out that rapid loading of cuticles with solutes works only through their inner surfaces, where diffusion coefficients are much higher than in the outer surfaces.<sup>19</sup>

When the water of the sorption solution had evaporated, the sorption compartment was closed with a stainless steel cover held in position by a small amount of silicon grease. This helps to avoid radioactive spillage in case a cuticle breaks during desorption, and it maintain 100% humidity in the sorption compartments. The chambers were then placed, with the sorption compartment facing down, into the holes of a thick aluminum block thermostated at  $25 \pm 1^\circ\text{C}$ . This aluminum block was mounted on a rotary shaker that rocked the chambers horizontally during desorption at a frequency of about 60 cycles per minute. After temperature equilibration, 0.6 ml of PLS was added to each desorption chamber through the sampling port, using a syringe with a thin needle, and the shaker was activated. Desorption media were withdrawn quantitatively at 24 h intervals and were replaced by fresh PLS. After four successive samples had been taken, desorption was continued for an additional 4 d using 1% (w/v) aqueous surfactant solutions.

After termination of desorption, the covers were slipped off the sorption compartment, and the membrane areas exposed to the solutions were cut out carefully and placed in 5 ml of scintillation cocktail (Quickszint 212, Zinsser, Frankfurt am Main, Germany). After standing for 2 h, the radioactivity in the CMs was determined by scintillation counting (Packard CA 2000 scintillation counter). The high solubility of 2,4-D in this cocktail and the large mass of the cocktail relative to the mass of the cuticles ensured that all 2,4-D was quantitatively extracted by the cocktail, even from the thick pepper cuticles after 10 min (data not shown). The radioactivity in the desorption solutions was also determined after the addition of the cocktail (4 ml). All counting was performed at a  $2\sigma$  error of 1% and appropriate quench corrections were made.

The amount ( $M$ ) of radioactivity desorbed from each CM at any time ( $t$ ), denoted  $M_t$ , was obtained by summation of the radioactivities of successive samples. The total radioactivity initially contained in the CM ( $M_0$ ) was calculated as the sum of the amounts desorbed plus the amount of radioactivity left in the CM after termination of desorption. Thus, the ratio  $M_t/M_0$  represents the relative amount desorbed and  $1 - M_t/M_0$  is the relative amount of radioactivity in the CM at a given time  $t$ . These calculations were performed for each CM separately and the results plotted as  $\ln(1 - M_t/M_0)$  vs. time. Each treatment (type and concentration of surfactant) was replicated 20 to 40 times.

The slope of the plot  $\ln(1 - M_t/M_0)$  vs time is the first-order rate constant ( $k$ ) of the desorption process. It can be related to  $P^*$  as shown below.

It has been shown previously<sup>18,19</sup> that, structurally, cuticles are highly asymmetrical. They may be viewed as a laminate composed of a very thin outer layer (a "skin") having a low sorption capacity and a very low diffusion coefficient, and a thick inner layer with a high sorption capacity and a diffusion coefficient that is much higher than that in the skin. The inner compartment comprises most of the mass of the CM.

In UDOS, the inner sorption compartment is loaded with solute (2,4-D) and serves as the donor compartment. Diffusion of solute across the skin is rate limiting. The flow ( $F$ ) is

$$F = \Delta M / \Delta t = V_{\text{don}} (\Delta C / \Delta t) \quad (4)$$

where  $V_{\text{don}}$  is the volume of the donor compartment of the cuticle. If  $\Delta C$  changes with time, Equation 4 assumes the form

$$F = P^* A (C_{\text{don}} - C_{\text{rec}}) = -V_{\text{don}} (dC_{\text{don}}/dt) = V_{\text{rec}} (dC_{\text{rec}}/dt) \quad (5)$$

where  $A$  is the membrane area and  $P^*$  is the permeance. The asterisk is necessary to prevent confusing it with the permeance  $P$  calculated using the solution concentrations as driving force. The subscripts don and rec refer to the donor and receiver compartments, respectively. The integral solution of Equation 5 is

$$-P^* A (1/V_{\text{don}} + 1/V_{\text{rec}}) t = \ln(C_{\text{don}} - C_{\text{rec}})/C_0 \quad (6)$$

$C_0$  is the donor concentration when  $t = 0$ . If the receiver concentration can be maintained at zero, Equation 6 reduces to

$$-(P^* A / V_{\text{don}}) t = \ln C_{\text{don}} / C_0 = \ln(1 - M_t / M_0) \quad (7)$$

If  $\ln(1 - M_t/M_0)$  is plotted against  $t$ , a straight line having slope ( $k$ ) will be obtained and

$$k = -P^* A / V_{\text{don}} \quad (8)$$

Thus, from the first-order rate constant  $k$ , the permeance  $P^*$  can be calculated if  $V_{\text{don}}$  is known. Since the skins of the cuticles have a finite but negligible thickness, we have assumed that  $V_{\text{don}}$  is equal to the total volume of the CM of area  $A$ . We have further assumed that the specific gravity of the CM is unity and calculated  $V_{\text{don}}$  simply from the mass of the CM. Since the specific gravity of cuticles is somewhat larger than unity,  $V_{\text{don}}$  of *Citrus* CMs will be underestimated by about 5%.<sup>20</sup> If the mass of the skin is 5% of the total mass of the CM, the two errors will cancel.

These assumptions are not crucial, since the surfactant effect is estimated by comparing the rate constants of desorption obtained with PLS with those obtained using surfactant

TABLE 2  
Effects of Surfactants on Water Permeability of Cuticular  
Membranes from Leaves (*Citrus*, *Pyrus*) and Fruits (*Solanum*,  
*Capsicum*)

Surfactant	<i>Citrus</i>	<i>Pyrus</i>	<i>Solanum</i>	<i>Capsicum</i>
Water Permeability in m/s				
P(CM) $\times 10^{10}$	1.52	3.10	4.95	18.80
P(MX) $\times 10^7$	1.56	0.98	1.19	1.28
P(MX)/P(CM)	1026	316	240	68
Surfactant Effect on Water Permeability				
SDS	0.64—0.73	1.27—1.71	0.60—0.84	0.51—0.77
Triton X-100	2.46—3.16	5.63—9.17	1.24—1.70	2.30—2.88
Tween 85	2.78—3.95	6.54—7.96	1.93—2.53	2.22—3.22
Renex 36	4.49—7.13	20.14—42.38	2.56—3.58	2.48—3.92
Ethomeen T25	5.94—9.08	122.55—185.60	7.43—12.04	3.65—3.83
Brij 30	7.23—8.77	6.71—15.35	2.73—3.65	2.74—3.37

Note: Water permeances of CMs before treatment, P(CM), are means of 100 membranes; permeances of MX membranes, P(MX), are means of 10 membranes. Nominal surfactant coverage was 2 mg/cm<sup>2</sup>. The surfactant effect is the ratio of water permeances after and prior to surfactant treatment. The surfactant effect was calculated for each CM individually and was averaged for 10 to 15 CMs. The 95% confidence intervals are given. They represent the variability in response of individual CMs.

solutions. The errors will cancel as long as the thickness of the skin is not affected by the surfactants. This is not likely to happen, and we have found no indications for such an effect of surfactants.

### III. RESULTS

#### A. WATER PERMEABILITY

The effects of surfactants on the water permeability of the CMs depended on the type of surfactant and on the plant species (Table 2). SDS decreased the water permeability of *Citrus*, *Solanum*, and *Capsicum*, spp. CMs but slightly increased the permeability of some *Pyrus* CMs. All other surfactants increased the water permeability of the CMs of all four species, with Renex 36, Brij 30, and Ethomeen T25 being the most effective ones. The highest effects were always observed with CMs of pear leaves. Here, an increase in water permeability by factors of 122 to 185 was observed.

The effects of ethoxylated amines on the water permeability of *Citrus* CMs were very large and increased within each class (coco-, tallow-, oleyl-, and sterylamine) with increasing length of the oxyethylene chains. For a given degree of ethoxylation, the effect tended to increase with increasing length of the alkyl chains (Table 3). Ethomeen HT60 was almost ineffective.

Of the polyethylene glycols (PEGs) tested, the maximum effect was observed with PEG 400 (Table 4). PEG 4000 was ineffective.

When the time needed for evaporation of water from the treating solutions (*Citrus* CMs, 2 mg/cm<sup>2</sup> Renex 36) was varied, it was found that the effect was independent of the exposure time to micellar solutions in the range of 45 to 240 min. Longer time periods were not tried.



TABLE 3  
Effects of Ethomeen Surfactants on Water Permeability of  
*Citrus* Leaf Cuticular Membranes

Surfactant	nEO	Alkyl chain	Effect	95% CI
Ethomeen C12	1	C12 (50), C14 (20)	5.53	4.67—6.39
Ethomeen C15	5	C12 (50), C14 (20)	6.30	5.67—6.93
Ethomeen T15	5	C16 (31), C18 (64)	6.62	5.88—7.36
Ethomeen T25	15	C16 (31), C18 (64)	7.92	6.77—9.07
Ethomeen S15	5	C16 (14), C18 (80)	7.24	6.61—7.87
Ethomeen S25	15	C16 (14), C18 (80)	7.64	6.39—8.89
Ethomeen HT15	5	C16 (31), C18 (64)	7.51	6.57—8.45
Ethomeen HT25	15	C16 (31), C18 (64)	10.08	9.18—10.98
Ethomeen HT60	50	C16 (31), C18 (64)	1.35	1.29—1.40

Note: Average ethylenoxide residues (nEO), average alkyl chain-length distribution, and relative amounts in percent (in parentheses) were obtained from the manufacturer. The C<sub>18</sub> moiety of Ethomeen S15 and S25 is an oleyl rest. Water permeance of the CMs prior to surfactant treatment was  $1.82 \times 10^{-10}$  m/s. The effect of surfactant is the ratio of water permeance after and prior to surfactant treatment, calculated for each CM separately and averaged over 10 to 15 CMs per treatment. Nominal coverage was 2.0 mg/cm<sup>2</sup>. CI, confidence interval.

TABLE 4  
Effect of Polyethylene Glycols (PEGs)  
on Water Permeability of *Citrus* CM

Compound	nEO	Effect	95% CI
PEG 200	1—10(4)	1.73	1.63—1.83
PEG 400	3—20(9)	2.36	2.21—2.50
PEG 1000		1.61	1.36—1.86
PEG 4000		0.95	0.90—1.10

Note: Range of number of ethylene oxide (nEO) residues and most frequent homologue according to Engle et al.<sup>3</sup> Water permeance of the CMs prior to treatment was  $1.98 \times 10^{-10}$  m/s. The effect is the ratio of water permeance after and prior to treatment, with PEG calculated for each CM separately and averaged over 10 to 15 CMs per treatment. Nominal coverage was 0.2 mg/cm<sup>2</sup>. CI, confidence interval.

The effects of surfactants applied to the outer surfaces of *Citrus* CMs on water permeability were not completely reversible (Table 5). When the surfactants were washed off the surfaces of the CMs, a significant residual effect on water permeability remained. The residual effect of Triton X-100 was barely significant.

Oil in water emulsions of liquid paraffin with nonionic surfactants increased water permeability more than the surfactants alone (Figure 2). This effect was not significant at the 95% level for all emulsions, but the tendency was the same in all cases. Paraffin oil alone did not affect the water permeability of *Citrus* CMs the (95% confidence interval of the effect was 1.14 to 1.40). The action of surfactants and paraffin oil is therefore cooperative.

TABLE 5  
The Effect of Removal of Surface Residues of  
Surfactants on Water Permeability of *Citrus* CMs

Surfactant	Coverage (mg/cm <sup>2</sup> )	Effect (95% CI)	Residual effect (95% CI)
Triton X-100	2.0	2.23—3.48	1.27—1.59
Renex 36	0.5	3.39—3.89	1.73—2.30
Brij 30	2.0	5.87—8.87	2.50—3.69

Note: Water permeance of the CMs prior to surfactant treatment was  $2.05 \times 10^{-10}$  m/s. The effect of surfactant is the ratio of water permeance after and prior to surfactant treatment, calculated for each CM separately and averaged over 10 to 15 CMs per treatment. After the effect had been determined, the surfaces of the CMs were washed extensively with water to remove the surface residues of surfactants, the chambers were filled with fresh water, and the permeance was determined again. The residual effect is the ratio of the permeances after washing the CMs over the permeances of untreated CMs. Nominal coverages given. CI, confidence interval.

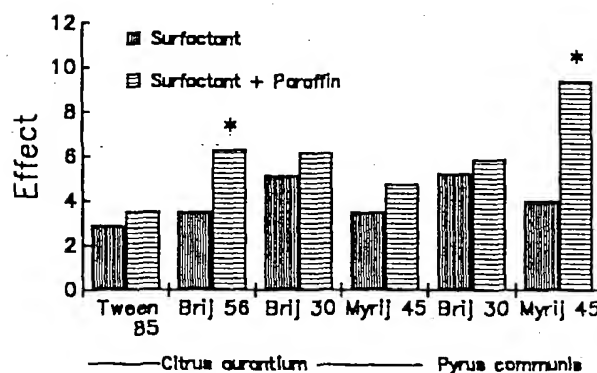


FIGURE 2. Effects of surfactants and surfactant/paraffin oil emulsions on water permeability of *Citrus* and pear leaf CMs. Nominal coverage was 0.6 mg/cm<sup>2</sup> for the surfactant treatment and 0.6 mg/cm<sup>2</sup> surfactant plus 1.4 mg/cm<sup>2</sup> paraffin oil for the emulsion. The effect is the ratio of water permeances after and prior to treatment. The effect of the emulsion is larger than the effect of the surfactant alone when marked with an asterisk (at the 95% level).

#### B. SURFACTANT EFFECTS ON 2,4-D PERMEABILITY OF POLYMER MATRIX MEMBRANES

Triton X-100 increased the 2,4-D permeance of green pepper MX membranes when present in the donor solution at a concentration of 0.01% (Figure 3A). Higher concentrations decreased 2,4-D permeance. At 25°C, the CMC of Triton X-100 is 0.019% (w/v)<sup>23</sup> This decrease in permeance at Triton X-100 concentrations above the cmc is caused mainly by the decrease of the MX/water ( $K_{mx/w}$ ) partition coefficient of 2,4-D. Below the cmc, there was no effect of Triton X-100 on ( $K_{mx/w}$ ) (Figure 3B). Triton X-100 slightly increased 2,4-D mobility ( $P^*$ ) in green pepper MX membranes when present at concentrations of 0.3% (Figure 3C).



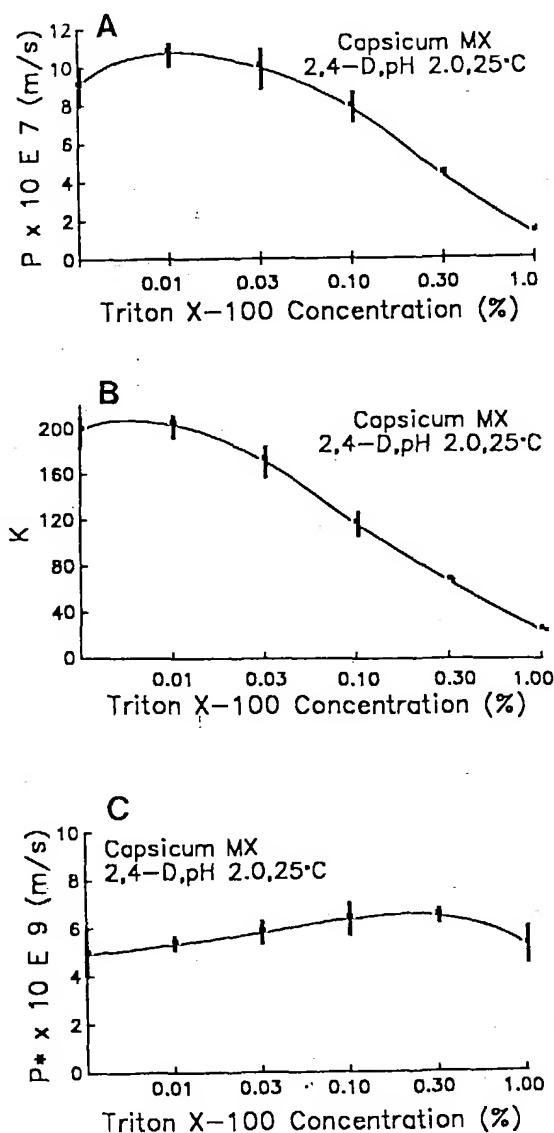


FIGURE 3. The effect of Triton X-100 on 2,4-D permeability of green pepper MX membranes. The surfactant was added to the donor.

Polydisperse <sup>3</sup>H-labeled Triton X-100 penetrated green pepper MX membranes. The permeance measured using a donor concentration of 0.01% (w/v) amounted to  $1.40 \times 10^{-7}$  m/s (confidence interval =  $0.92$  to  $1.16 \times 10^{-7}$  m/s),  $K_{mx/w}$  was 108 (CI = 95 to 121), and  $P^*$  was  $1.03 \times 10^{-9}$  m/s (CI =  $0.91$  to  $1.13 \times 10^{-9}$  m/s).

### C. SURFACTANT EFFECTS ON 2,4-D PERMEABILITY OF CUTICULAR MEMBRANES

Surfactants in the donor in concentrations above the cmc will invariably result in reduced permeances when solutes interact with surfactant micelles. Micelles compete with cuticles as sorption compartments; the concentration of 2,4-D in the cuticles and the partition coef-

ficient decrease, and therefore  $P$  as well (Figure 3). As a consequence, surfactant effects on permeance can be analyzed only when their effects on the partition coefficients are measured simultaneously.

This problem does not arise when surfactants are added to the receiver solutions, provided the solute concentration in the receiver is maintained of practically zero. In this case, there will be no effect of surfactants on the driving force (the concentration gradient in the membrane) and any effects observed will be mobility effects.

To study the influence of surfactants on the mobility of 2,4-D in CMs, the cuticles were first loaded through the inner surfaces with 2,4-D in a sorption experiment. The 2,4-D was then desorbed through the outer surfaces, using an inert desorption medium. Initially, we used a borax buffer in which 2,4-D was fully ionized, the concentration of nonionized 2,4-D was therefore zero at all times. This, however, would work only with solutes that were weak acids. To make the test more general, a lecithin suspension was used as a desorption medium instead of borax buffer. The lecithin aggregates are large and do not penetrate the CM, but they serve as sorption compartments for lipophilic solutes. This keeps their concentration in the surrounding water practically zero. A comparison of the two desorption media using paired observations gave identical results. Phospholipid suspensions were ineffective in the transpiration test (data not shown).

UDOS of 2,4-D using a 1% phospholipid suspension (PLS) resulted in straight lines when results were plotted as a first-order rate process (Figure 4). The amounts and concentrations of 2,4-D sorbed in the CMs decreased exponentially with time. The slopes of the lines are the first-order rate constants of this process.

The effects of surfactants on this desorption process were investigated using the method of paired observations. The rate constant of desorption using PLS were established for each CM first. Then desorption was continued using micellar solutions of surfactants. The effects of the surfactants tested can be grouped as follows. (1) With SDS as description medium (Figure 5A), either no significant change in slopes was observed or the change was small and instantaneous. (2) With Ethomeen T25, the change in slopes was large, occurred rapidly, and the slopes remained linear until the experiment was terminated (Figure 5B). (3) Desorption with Triton X-100 resulted in curves having increasing slopes (Figure 5C). Desorption with Renex 36 at concentrations of 0.1% resulted in curves that resembled those in Figure 5C, but the time dependence of the slopes was more pronounced (Figure 5D).

All surfactants tested increased the rate constants of desorption of 2,4-D (Table 6). With most surfactants, the effect increased with time, and ranking of surfactants was done using the maximum effect. This is the ratio of the rate constant of desorption observed between the seventh and eighth day of experimentation and the rate constant between the first and fourth day using PLS. The mean maximum effect was very small with SDS, and increased in the other Triton X-100, Ethomeen T25, Brij 30, and Renex 36. Desorption with 1% Renex 36 increased the mean maximum rate constant of desorption by a factor of 16.64. The modes are in most cases smaller than the arithmetic means (negative excess), and the standard deviations, especially those of the means, are large.

The magnitude of the effect depended on the initial permeance ( $P^*$ ) as determined using PLS (Figure 6). The lower the initial  $P^*$ , the larger the effect of the surfactant on the rate constant. The effects observed for individual CMs ranged from a 2- to a 40-fold increase in  $P^*$  (Figures 6A to 6D). When the maximum effect of the surfactant was plotted against the reciprocal of the initial  $P^*$ , a weak but significant correlation was obtained for all surfactants except the inert anionic SDS.

#### IV. DISCUSSION

Surfactants can markedly increase the permeability of plant cuticles for both water and solutes. How this is accomplished is the main topic of this section.

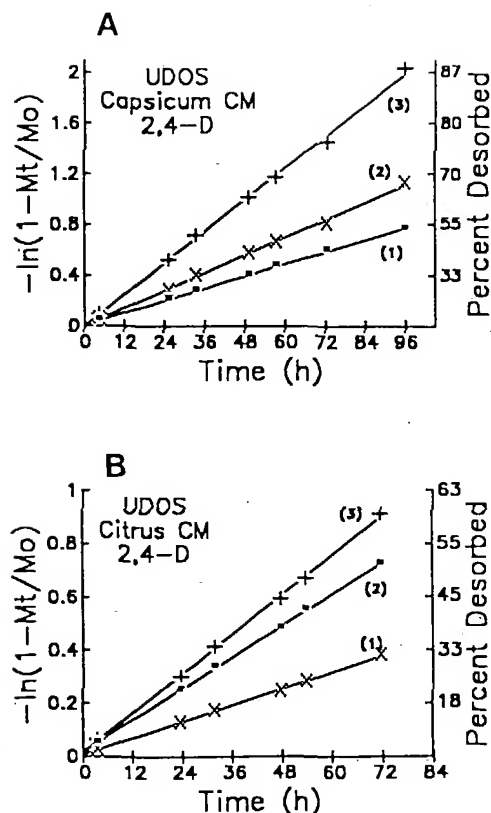


FIGURE 4. Unilateral desorption of 2,4-D from the outer surface of Citrus CMs using a 1% phospholipid suspension.

The barrier limiting the transport of water and solutes across CMs is located at the air/cuticle interface. It is a solid-state barrier composed of cutin and soluble cuticular lipids (waxes). The waxes are microcrystalline, and the crystallites represent excluded volumes for the diffusion of solutes and water because they are (on a short time scale) inaccessible. Diffusion is restricted to amorphous regions and to crystal/cutin interfaces.<sup>14,19</sup>

In homogeneous membranes, the permeability coefficient ( $p$ , the permeance of a membrane of unit thickness) is the product of the partition ( $K$ ) and the diffusion coefficient ( $D$ ) in the membrane:<sup>2</sup>

$$p = D \times K = P^* \times \ell \times K \quad (9)$$

Thus, there are three ways in which surfactants can affect the permeability of CMs to water and solutes: they can affect either  $K$ ,  $D$ , or both. When permeance is calculated using the solute concentration in the cuticle as the driving force,  $P^* \ell$  is equivalent to  $D$  (Equations 3 and 9). The sites of action can be cutin, amorphous waxes, or the cutin/wax interfaces.

Surfactant effects on cutin or the polymer matrix are easy to understand. Surfactants in the donor at concentrations above the cmc will reduce the cuticle/water ( $K_{m/w}$ ) partition coefficient for the solute, and hence will reduce the permeance proportionately (Figure 3). This  $K$ -depression is due to solubilization of the solute molecules in micelles, and for a given surfactant it increases with increasing number of micelles, that is, with increasing concentration of surfactant. The  $K$ -depression also depends on the solubilization capacity

TABLE 6  
Effects of Surfactants on Rate Constants of Desorption  
(UDOS) of 2,4-D from *Citrus* Cuticular Membranes

Surfactant	n	Initial $P^* \pm SD$ ( $\times 10^{12}$ m/s)	Effect	
			Mean $\pm SD$	Median $\pm SD$
SDS	25	$2.99 \pm 0.85$	$1.73 \pm 0.45$	$1.67 \pm 0.09$
Triton X-100	38	$3.36 \pm 1.31$	$5.26 \pm 2.57$	$4.41 \pm 0.42$
Ethomeen T25	30	$2.00 \pm 0.73$	$10.17 \pm 4.59$	$10.24 \pm 0.85$
Brij 30	22	$2.13 \pm 1.18$	$13.47 \pm 5.22$	$12.42 \pm 1.11$
Renex 36	29	$2.76 \pm 2.12$	$16.64 \pm 9.67$	$16.50 \pm 1.60$

Note: The initial  $P^*$  is the permeance measured using PLS. It was calculated from the rate constant of desorption according to Equation 8. The effect is the ratio of the rate constants measured during the last desorption period (day 7 to day 8) with surfactant to the rate constant measured using PLS. It represents the maximum increase in rate constant or permeance observed. The number of CMs studied (n) and standard deviation (SD) are given. Surfactant concentration was 1% (w/v).

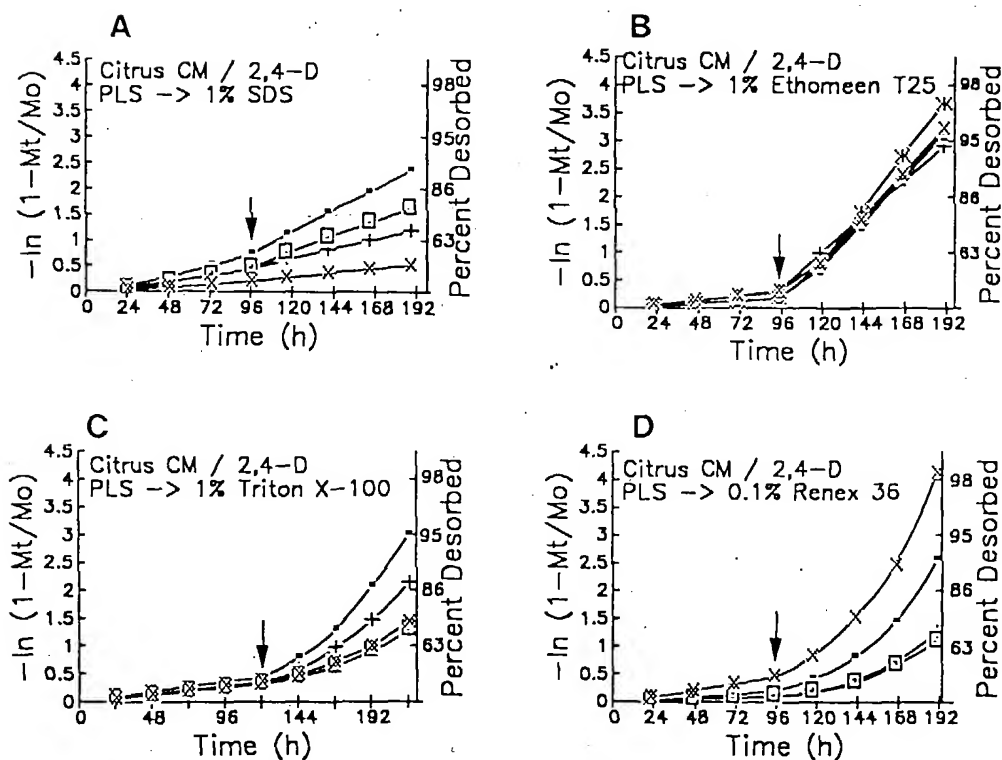


FIGURE 5. Unilateral desorption of 2,4-D from the outer surface of *Citrus* CMs. Up to 96 h, the desorption medium was a 1% phospholipid suspension (PLS); 1% surfactant solutions were used between 96 and 192 h.

of a given surfactant for a given solute.<sup>9</sup> For polar solutes, which are not solubilized in micelles, the K-depression will be absent, but with lipophilic solutes, the K-depression will invariably slow penetration by decreasing  $P$ . The magnitude of this K-depression will depend on the type of solute, type of surfactant, and its concentration.<sup>9</sup>

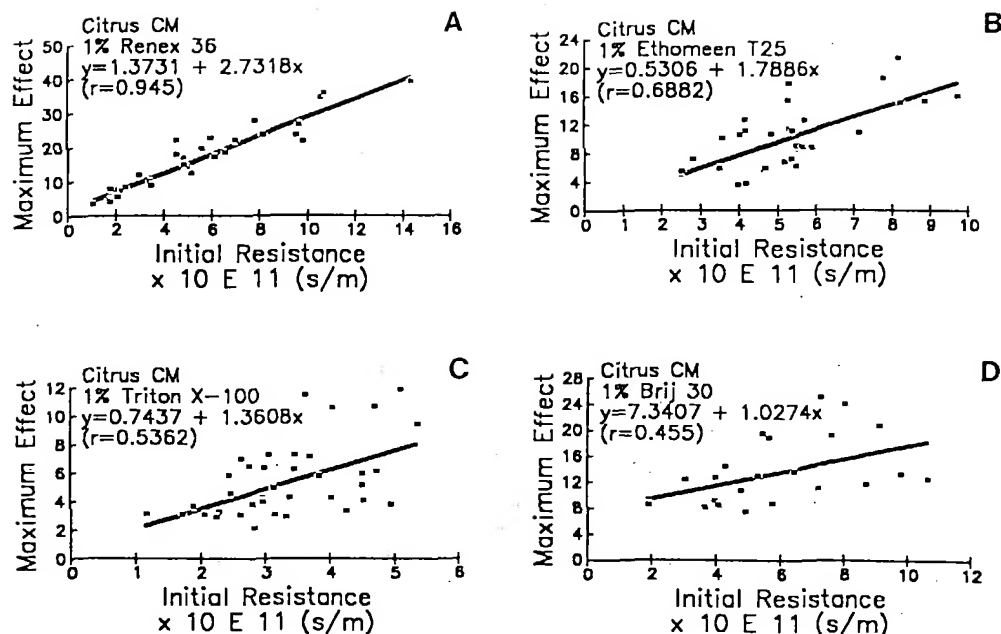


FIGURE 6. Correlation of initial 2,4-D resistance of *Citrus* CMs with the maximum effects of surfactants on rate constants of desorption in UDOS. Initial resistance is the reciprocal of initial permeance ( $P^*$ ) determined using 1% PLS. The effect is the ratio of maximum rate constants measured using surfactant solutions for desorption over the rate constants observed using PLS.

Depending on surfactant concentration (Figure 3), a small effect on solute mobility in the polymer matrix can be observed. This slight increase in  $P^*$  indicates an increase in polymer chain mobility. However, 2,4-D permeance was much more affected by the  $K$ -depression than by an increase in  $P^*$  as long as the surfactant concentration was above the cmc. Below the cmc, there was no surfactant effect on  $K_{mx/w}$ , and a slight increase in  $P^*$  was the sole effect of Triton X-100 (Figure 3A).

A surfactant effect on  $P^*$  requires that the surfactant be present in the polymer matrix. This poses no serious problems, since nonionic surfactants are soluble in cuticles.<sup>21</sup> Our data for green pepper MX membranes also show a good solubility of Triton X-100 ( $K_{mx/w} = 108$ ). In equilibrium with a Triton X-100 solution of 0.01%, the MX contained 10.8 g of Triton X-100 per kilogram of MX. The 2,4-D concentration in the MX of experiments shown in Figure 2 and Table 6 amounted to only  $7 \times 10^{-3}$  g of 2,4-D per kilogram of MX. This means that for every 2,4-D molecule in the MX there were about 550 molecules of Triton X-100.

Analyzing surfactant effects on the permeability of CMs is more difficult. The analysis must again center around the surfactant effects on  $K$  and  $P^*$ , but interactions between surfactants and waxes must also be considered. Using CMs from *Citrus* and pear leaves, Riederer and Schönherr<sup>16</sup> have shown that aliphatic constituents of cuticular waxes (alcohols, alkylesters, and alkanes) were neither dissolved nor solubilized by copious quantities (2 mg/cm<sup>2</sup>) of SDS, Triton X-100, Brij 30, Tween 85, Renex 36, and Ethomeen T25. Hence, the effects of these surfactants on water and solute permeability demonstrated in this study cannot be attributed to the loss of these types of soluble cuticular lipids. In the next analysis, we shall discuss surfactant effects on water and solute permeabilities separately, because experimental conditions and surfactant action in the transpiration test and in UDOS are not completely comparable.

The fact that UDOS resulted in straight lines when  $\ln(1 - M_t/M_o)$  was plotted against time (Figure 3) shows that the assumptions inherent in Equations 4 to 8 are valid. 2,4-D sorbed in the inner regions of the CM diffuses across the rate-limiting skin into the receiver solutions, where it is trapped in either the PLS or the surfactant micelles. This linearity is evidence that the diffusion coefficient in the limiting skin is much lower than in the sorption compartment. Thus, diffusion of 2,4-D in the inner sorption compartment is not rate limiting. It is diffusion in the skin that is rate limiting. The rate constants obtained using UDOS therefore represent transport properties of the skin rather than those of the entire CM.

UDOS has a number of properties that make it well suited to quantifying and analyzing surfactant effects on solute permeation in the limiting skin of cuticles. (1) The driving force is the solute concentration in the cuticle rather than the concentration gradient between donor and receiver solutions. This eliminates the effect of surfactants on the partition coefficient (K-depression). (2) The effects of surfactants are measured for each CM individually because UDOS uses the method of paired observations: each CM is control (desorption with PLS) and treatment (desorption with surfactant). This makes the test very sensitive, as it eliminates the effects of natural variability of permeabilities among CMs. It also provides the possibility of correlating surfactant effects with the permeance of untreated CMs (initial permeance), as shown in Figure 6. (3) Surfactant effects can be quantified using rate constants which are obtained without making any assumptions. (4) Even the assumptions needed to calculate  $P^*$  do not cause problems when permeances of different solutes or effects of different surfactants on permeance for a given type of cuticle are compared. In all of these cases, the assumptions concerning the size of  $V_{don}$  will cancel. (5) For a given type of CM,  $P^*$  is equivalent to  $D$  (Equation 9), it is essentially a mobility, and any surfactant effect observed with UDOS is an effect on mobility.

All surfactants tested using UDOS had a large effect on the mobility of 2,4-D in *Citrus* CMs (Table 6). SDS was the only exception, and its small effect can be considered negligible. Effects that are rate constants increased with time (Figure 5) until the experiments were terminated. It was not possible to continue desorption with surfactants because there was very little 2,4-D left in the CMs after 4 d of desorption with surfactant solutions (Figure 5). With these surfactants, maximum effects could not be determined. This indicates that surfactant penetration into the cuticles was very slow, and equilibrium between desorption media and cuticles was not obtained in 4 d. The maximum effect of Ethomeen T25 was obtained rapidly, after only 1 to 2 d (Figure 5).

Surfactant effects were inversely related to the initial resistance ( $1/P^*$ ) of the CMs (Figure 6). The mobility of 2,4-D in CMs having a low initial permeance was much more affected by surfactants than in CMs having a high initial permeance. It remains to be seen if surfactant effects on the solute permeances of cuticles from other species having much higher initial permeances than *Citrus* CMs will also be smaller.

Since surfactant effects were dependent on time and initial permeance, it is difficult to rank surfactants according to activity. If one uses the maximum effects observed (which are not identical to the maximum effects possible, except for Ethomeen T25) as a criterion, the sequence of increasing activity was Triton X-100, Ethomeen T25, Brij 30, and Renex 36. HLB values of these surfactants ranged from 9.8 to 19.3 (Table 1).

The time dependence of the surfactant effect in UDOS is evidence that surfactants must penetrate the skin of the CM to be effective. For an effect located at the very surface of the CM, an immediate response would be expected. Penetration of surfactant monomers into the CM seems to be a slow process since, with most surfactants, effects increased from the first to the fourth day. This is not surprising, since diffusion coefficients of solutes in cuticles depend heavily on molar volumes<sup>19</sup> and ethoxylated surfactants are rather large molecules. This effect of surfactant size on permeance can be seen by comparing the permeances of

2,4-D and Triton X-100 in green pepper MX. The permeance of 2,4-D was 5.4 and  $P^*$  was 4.8 times larger than for polydisperse Triton X-100. This difference is likely to be even larger in CMs.

The relationship between surfactant effects on the mobility of 2,4-D in the skin of CMs and the concentration of the surfactant there cannot be deduced from our data. Before our results can be fully understood, sorption in and permeance of surfactants across CMs must be studied in relation to surfactant properties.

Our results and the above discussion show that at least four parameters are needed to quantitatively describe the activity of surfactants on solute mobility in cuticles. (1) The effect depends on the concentration of the surfactant in the cuticle. The cuticle/water partition coefficient together with concentration of surfactant monomers in the aqueous phase quantitatively account for this effect. (2) The surfactant must enter the cuticle, and if permeation occurs through the outer skin (as in actual practice), this will be a slow process determined by the diffusion coefficient in the cuticle (or by  $P^*$ ) and by the driving force. (3) The interactions between surfactants, cutin, and amorphous waxes that lead to increased mobility of solutes must be suitably quantified, possibly by a parameter related to segmental chain mobility in cutin and in amorphous waxes. (4) If surfactant effects depend on surfactant-solute interactions and not only on surfactant-cuticle interactions, this effect will have to be accounted for by yet another parameter. This argument will not be discussed further, since all surfactants were polydisperse. We do not know which homologues were active and to what degree. To answer these questions and to analyze structure-activity relationships in UDOS, the effects of monodisperse surfactants in UDOS must be studied. Since water and solutes have to overcome the same barrier in cuticles, one might expect that the surfactant effects on solute and water permeability are the same, providing the surfactants affect water permeability solely by affecting the mobility of water in the skin.

The transpiration test was initially designed to screen surfactants for effects on water permeability.<sup>4</sup> The aim was to distinguish between active and inactive surfactants. The magnitude of the effect was less important. In the present study, we had the same goal, and this is why we used very high coverages (2 mg/cm<sup>2</sup>) for screening surfactants.

Ethoxylated surfactants are sorbed in cuticles.<sup>21</sup> The polyoxyethylene chains of sorbed surfactants are probably hydrated. This increases the water concentration in the CMs, and the effect of surfactants is therefore a mixed effect: both the mobility ( $D$ ) and the partition coefficient of water in the cuticles are likely to be increased by active surfactants. These two effects cannot be separated unless the amounts of surfactant sorbed in the CM and the amount of water associated with the polyoxyethylene chains are known. This is not the case at the present time, and the surfactant effects on water permeability shown in Tables 2 through 4 cannot be fully analyzed.

All active surfactants are technical products and polydisperse. The effects observed are averages of the effects of individual homologues. These homologues differ in ethoxylation, and thus in polarity and in molecular weight. Their partition and diffusion coefficients in cuticles will differ. It is therefore no meaningful to attempt to correlate surfactant structure to activity in the transpiration test using our data obtained with polydisperse surfactants. For this type of analysis, the effects of monodisperse surfactants on the water permeability of CMs are needed. A few general points can be made, however.

1. Ethoxylation seems to be necessary for activity. Even PEGs were active (Table 4). The activity seems to depend on the mole ratio of hydrophobe and polyoxyethylene chains (Table 3). However, there was no clear relationship between HLB and the activity of surfactants. Very active surfactants had HLB values ranging from 10 (Brij 30) to almost 20 (Ethomeens). Excessive size (Ethomeen HT 60, PEG 4000) seems



- to prevent activity, possibly because these very large molecules cannot penetrate the cuticles. SDS is small, but negatively charged, very polar, and therefore not sorbed in the CMs. It is inactive because it cannot enter the CMs.
2. Surfactant effects on water permeability were only partially reversible (Table 5). Since cuticular waxes are not dissolved or solubilized by these surfactants,<sup>16</sup> this residual effect indicates that the surfactants had not been washed out completely. In fact, the surfactants were detected in cuticular waxes extracted from cuticles that had been treated similarly.<sup>13</sup>
  3. Surfactant effects were larger with UDOS than in the transpiration test. 2,4-D molecules are much larger than water molecules and they experience much more hindrance in the CMs than water. In fact, the permeance of 2,4-D in *Citrus* CMs is about  $6 \times 10^{-10}$  m/s (calculated as  $P^* \times K$ , using the data of Table 6 and a  $K$  of 300),<sup>15</sup> while water permeance is  $1.5 \times 10^{-10}$  m/s (Table 2). It therefore seems that larger molecules benefit much more from surfactant effects than smaller ones. This agrees with the observation that 2,4-D mobility in CMs was much more affected by surfactants when the initial permeance was low (Figure 6).
  4. Differences in the magnitudes of surfactant effects between the two tests may also be due to different states and concentrations of surfactants in the two types of experiments. In the transpiration test, the surfactants occur as a highly concentrated phase on the surface of the cuticles. The proximity of the dry silica gel and the low water permeances of most cuticles will result in very low water content of the neat surfactant phase. With *Citrus* and pear leaf CMs, the surfactant phase was thicker than the CMs themselves, which had an average mass of only 0.25 mg/cm<sup>2</sup>. In UDOS, surfactants were used as diluted micellar solutions. This difference will lead to different (but unknown) concentrations of surfactants in the cuticles and hence to different effects.
  5. The sequence of effectiveness with *Citrus* CMs was similar in both types of tests: SDS was almost ineffective, Triton X-100 had the lowest effect, and Brij 30, Ethomeen T25, and Renex 36 were the most effective. It appears that the hydration water of surfactants sorbed in the cuticles did not contribute greatly to the total effect of surfactants in the transpiration test. Thus, both tests are suitable for screening surfactants for activity. They may also be used to test emulsions (Figure 2) or complete formulations.

We shall employ the tests in the future to investigate structure-activity relationships using monodisperse surfactants. To the manufacturers of pesticides, the tests can be useful tools for screening formulations for their effectiveness in increasing the mobility of active ingredients in cuticles. This will help to better understand the complex results obtained in field trials or with droplet experiments. The outcomes of these experiments depend on many factors, such as wetting, spreading, retention, coverage, state of surface residue, volatility of active ingredients, partitioning of active ingredients, and diffusion across the cuticles. All these factors are affected by surfactants. With UDOS, the effects of surfactants on the mobility of active ingredients in cuticles can be measured specifically without interference by the factors mentioned above.

### ACKNOWLEDGMENT

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## Chapter 3

**RELATIONSHIP BETWEEN SURFACTANT PROPERTIES AND  
WETTABILITY OF RICE LEAF SURFACES FOR SEVERAL  
NONIONIC SURFACTANTS****B. J. Chung and Y. W. Kwon****TABLE OF CONTENTS**

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## ABSTRACT

The wettability of several important nonionic surfactants on rice leaf surfaces was examined at the active tillering, and heading stages for eight rice varieties differing widely in characteristics of leaf morphology. Surfactants were chosen from homologous series of polyoxyethylene (POE) nonylphenyl ethers (NP), POE octylphenyl ethers (OP), POE sorbitans (sorbitans), and polystyrenated phenols (SP) having different ethylene oxide (EO) content and hydrophile-lipophile balance (HLB) value.

Scanning electron micrographs showed noticeable differences in the fine morphology of the leaf surface, particularly epicuticular wax deposits, among the varieties. The glabrous varieties had a denser wax coverage than the long-hairy and the pubescent, while the water wettable had the least wax coverage.

The contact angle on the leaf surface increased with an increase in the HLB value and logarithmically with an increase in surface tension. At HLB values of 12 to 13, the surface tension of the surfactants and the contact angle on the leaf surfaces showed the lowest value and adhesional force the highest value. Comparing surfactant groups, NPs and OPs had lower surface tension and contact angle, and higher adhesional force than sorbitans and SPs. Contact angles were lower, but adhesional forces were higher at the heading stage than at the tillering stage. Growth stage-dependent difference in adhesional force at a surface tension of 35 dyn/cm was not observed with NPs and OPs having HLB values of 12 to 13. Adhesional forces were related to contact angles ( $r = 0.948^{**}$ ) for all eight varieties at both growth stages.

For the eight varieties, contact angle increased more on water-wettable leaf surfaces than on glabrous, long-hairy, or pubescent leaf surfaces, but adhesional forces decreased less as surface tension increased. These results suggest that the wettability of rice leaf surfaces varies mainly with the degree of wax coverage of the rice varieties and with the particular growth stage.

From the above, it is concluded that adhesional force is a better criterion than contact angle in selecting for increased wettability of rice leaves.

## I. INTRODUCTION

In order to control pests effectively, pesticides sprayed onto plants must be taken up and subsequently translocated to the active site.<sup>18</sup> Uptake into plants is dependent on spray retention and spreading on plant surfaces.<sup>17</sup> Effective spray retention is known to be enhanced by good wetting of plant surfaces.<sup>2,3</sup>

Epicuticular waxes, trichomes, various hairs, and other protuberances of the leaf surface are known to act as barriers to pesticide uptake. The addition of surfactant is necessary to provide adequate wetting.<sup>4,6,9,12</sup>

Surfactants have often been classified according to their hydrophile-lipophile balance (HLB), moles of ethylene oxide (EO), and/or surface tension of dilute solution. In terms of the wettability of a surfactant solution, evaluations have been made according to the contact angle they form on target surfaces.<sup>1,4,5,8,11</sup> Since these criteria, but not the adhesional force, have been used rather exclusively to study the relationship between surfactants and target surfaces, it may be valuable to examine the significance of the adhesional force (surface tension multiplied by the cosine value of the contact angle) of surfactant solutions on intact rice (*Oryza sativa* L.) leaf surfaces.

The present study was carried out to establish guidelines for the proper selection of nonionic surfactants in the formulation of pesticides for rice culture. We were interested in elucidating the relationship between surfactant properties and the wettability of rice leaf

TABLE 1  
Rice Varieties Used in the Present Study

Variety	Source	Leaf surface property	Type
M 101	Cultivar of U.S.A.	Glabrous	Japonica
wx 817	wx 817-1-65-2-1	Glabrous	Tongil*
LK 2-7	LK2-7-12-1-1	Long-hairy	Japonica
HP 914	HP 914-3-2-1-1	Long-hairy	Tongil
Chucheong	Cultivar of Korea	Pubescent	Japonica
Cheongcheong	Cultivar of Korea	Pubescent	Tongil
HP 854	HP 854-8-1-2-8-1-1	Water wettable	Japonica
wx 139	wx 139-3-64-2-3-1-1	Water wettable	Tongil

\* Variety bred through crosses of Japonica and Indica varieties.

surfaces for several important nonionic surfactants. Rice varieties differing widely in gross leaf morphology and genetics (so-called glabrous, long-hairy, pubescent, or water-wettable leaf properties for Japonica and Indica  $\times$  Japonica types) were studied. The wettability of rice leaf surfaces was examined at the active tillering and heading stages with surfactants having different HLB and EO molar values.

## II. MATERIALS AND METHODS

### A. PREPARATION OF RICE LEAVES

The eight rice varieties used herein differed widely in the gross morphology of their leaf surfaces and were obtained from the Crop Breeding Laboratory of the Agronomy Department, Seoul National University and Crop Experiment Station of Korea. Table 1 shows the source, leaf surface property, and varietal type of the varieties used. They were cultured in ordinary paddy fields at the Hannong Central Research Institute.

### B. SCANNING ELECTRON MICROSCOPY (SEM)

Rice leaf sections of 5 cm were taken from the center of a flag leaf. The sections were dehydrated using the Gabriel method<sup>5,7</sup> and then dried by the critical point drying method.<sup>7</sup> The samples were coated by the U-520 (Polaron, England) at 18 mA,  $10^{-2}$  to  $10^{-4}$  mbar for 120 s. The Hitachi Model S-570 SEM was used to observe specimens at an accelerating potential of 24 kV. SEM photographs were taken for both sides of the same leaves at a magnification of 500 and 5000.

### C. PREPARATION OF SURFACTANT SOLUTIONS

The nonionic surfactants used in this study are listed in Table 2. All surface tension and contact angle measurements were made using a 0.1% (w/v) solution of the surfactants.

### D. MEASUREMENT OF SURFACE TENSION

The surface tension of each solution was measured by counting droplets with a 5-ml droplet-counting apparatus and then calculated by the formula:<sup>10</sup>

$$rl = \frac{no}{n} \times rw$$

where  $rl$  is the surface tension of a surfactant solution;  $no$ , the number of droplets of distilled water;  $n$ , the number of droplets of the surfactant solution; and  $rw$ , the surface tension of distilled water at 25°C. Each measurement was replicated three times.

TABLE 2  
Physicochemical Characteristics of the Nonionic Surfactants Used

Product name	Chemical description	Mol No. of EO	HLB	Supplier
Koremul NP-4	POE nonylphenyl ether	4	8.9	HNCI
Koremul NP-6		6	10.9	
Koremul NP-8		8	12.3	
Koremul NP-10		10	13.3	
Koremul NP-16		16	15.0	
Koremul NP-20		20	16.0	
Koremul NP-30		30	17.1	
Triton X-45	POE octylphenyl ether	5	10.4	R & H
Koremul OP-8		8	12.4	HNCI
Triton X-100		9—10	13.5	R & H
Triton X-102		12—13	14.6	R & H
Triton X-305		30	17.3	R & H
Tween 85	POE sorbitan triolate	20	11.0	Reagent
Tween 21	POE sorbitan monolaurate	4	13.3	
Tween 80	POE sorbitan monooleate	20	15.0	
Tween 20	POE sorbitan monolaurate	20	16.7	
SP 310F	Polystyrenated phenols	—	13.1	HNCI
SP 311F		—	13.3	
SP 309F		—	15.8	
Triton CS-7	Mixture of Triton X-114 (36) and Triton GR (5 M, 24%)		12.2	HNC

Note: EO, ethylene oxide; HLB, hydrophile-lipophile balance; HNCI, Hannong Chemical, Inc.; HNC, Hannong Corporation; R & H, Rohm & Haas.

### E. MEASUREMENT OF CONTACT ANGLE

A 2- $\mu$ l droplet of surfactant solution was applied to intact fresh rice-leaf blades mounted on glass slides with double-stick tape, using a micropipette fitted with a syringe needle (10  $\mu$ l, Hamilton). Pictures of the droplet on the intact leaf surface were taken (under reflected light) 2 min after each application with a Nikon FG 54-mm camera equipped with a close-up lens. The contact angle of the droplets was determined by projection/magnification on a screen. Each measurement was replicated three times.

#### Calculation of adhesional force

Adhesional force ( $W_a$ ) was calculated by the formula:<sup>10</sup>

$$W_a = rl \times \cos \theta$$

where  $rl$  is the surface tension of the surfactant solution (0.1% w/v), which equals the contact angle,  $\theta$ , of the droplet of surfactant solution on the rice leaf surface.

## III. RESULTS AND DISCUSSION

### A. FINE MORPHOLOGY OF LEAF SURFACE AND EPICUTICULAR WAXES OF RICE VARIETIES

SEM photographs showed noticeable differences in the fine morphology, especially of epicuticular wax deposits, of the leaf surface in the varieties examined. In the glabrous rice varieties, bicellular microhairs and small papillae protruded over the entire leaf surface (Figure 1). Long hairs and unicellular microhairs were seen in the long-hairy rice varieties (Figure 2). In the pubescent rice varieties, unicellular and bicellular microhairs, small papillae, large inflated papillae, and trichomes protruded over the leaf surface (Figure 3).

Bicellular microhairs, small papillae, and large inflated papillae were seen in the water-wettable rice varieties (Figure 4). The epicuticular wax deposit was platelet-shaped and deposit on the cuticle layer. Similar observations were previously made by Takeoka et al.<sup>19</sup> The glabrous varieties had a more dense coverage of epicuticular waxes than the long-hairy and pubescent varieties, while the water-wettable rice varieties had the least coverage. Epicuticular waxes are an important barrier to the wetting of the leaf surface, and in this study wettability seemed to be dependent on the degree of wax coverage on the leaf surface.

## B. RELATIONSHIP BETWEEN THE SURFACTANT PROPERTIES AND WETTABILITY OF NONIONIC SURFACTANTS

Low surface tensions were obtained for surfactants in the range of 12 to 14 HLB values, regardless of the number of moles of EO and the surfactant groups (Figure 5). It is well known that interfacial tension between the spray solution and plant surface must be reduced to aid wetting and the penetration of pesticides into leaves,<sup>3,8,13-15,17</sup> indicating that reduced surface tension increases the wettability of spray solutions. The HLB values of nonionic surfactants commonly used in agrochemical formulations have been reported to be in the 12 to 15 range.<sup>11</sup> Our results seem to justify this practice.

With respect to surfactant groups, NPs and OPs had lower surface tension than the sorbitans and polystyrenated phenols. Our results show that NPs and OPs having HLB values in the 12 to 14 range reduce surface tension more effectively than other surfactants.

Contact angles were low for surfactants having HLB values of 10 to 13. They were also lower at the heading stage than at the tillering stage (Figure 6). NP-8 and NP-10, and X-45 and OP-8, having low contact angles and surface tension among nonionic surfactants, all had HLB values of 12 to 14 (Figure 6).

As shown in Figure 7, contact angle increased logarithmically with an increase in surface tension. At the heading stage, a significant relationship between contact angle and surface tension was obtained:  $Y$  (contact angle) =  $160 \ln X - 560.5$  ( $r = 0.848^{**}$ ). Likewise, the relationship at the tillering stage was  $Y = 160.1 \ln X - 528.6$  ( $r = 0.831^{**}$ ).

Exceptionally, NP-4 and NP-6, marked by circles in Figure 7, had a low contact angle even though they had high surface tension. This may be due to the fact that these surfactants have poor water solubility and better compatibility with the intact leaf surface due to their lipophilic properties.

Adhesional forces generally decreased with an increase in the HLB value, showing high values in the 12 to 14 HLB range (Figure 8). Among surfactants having high adhesional force and low surface tension, NP-8 and NP-10, and OP-8 and X-100 all have HLB values between 12 and 14.

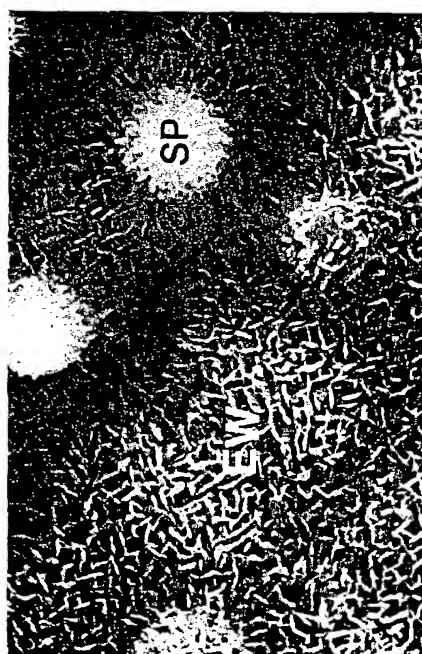
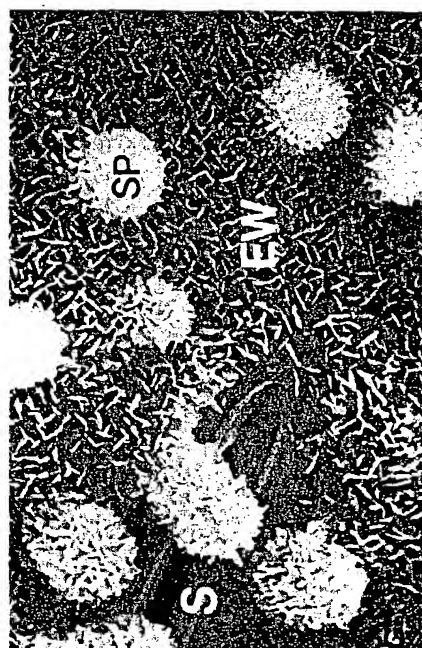
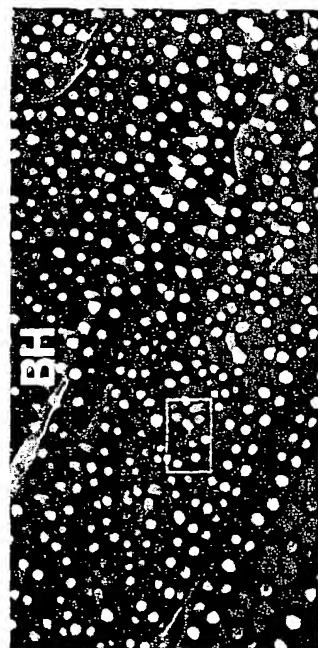
As shown in Figure 9, adhesional force decreased negatively with an increase in surface tension. At the heading stage, a significant relationship between adhesional force and surface tension was obtained:  $Y$  (adhesional force) =  $3596.7X^{-1} - 71.6$  ( $r = 0.826^{**}$ ). Likewise, the relationship at the tillering stage was  $Y = 4950X^{-1} - 113.5$  ( $r = 0.965^{**}$ ).

There were no growth stage-dependent differences in adhesional force at a surface tension of 35 dyn/cm, although growth stage-dependent differences in contact angle were observed at this surface tension (Figure 7).

Considering the growth-stage-dependent differences in contact angle, the use of intact rice leaves at the tillering stage, rather than at the heading stage, would appear to be better for evaluating the wettability of pesticide spray solutions.

Contact angles and adhesional forces had a significant logarithmic relationship with surface tension (Figures 10, 11). However, the correlation coefficients ( $r$ ) between adhesional force and surface tension ( $r = 0.879^{**}$  to  $0.903^{**}$ ) (Figure 11) were higher than those between contact angle and surface tension ( $r = 0.792^{**}$  to  $0.818^{**}$ ) (Figure 10). These

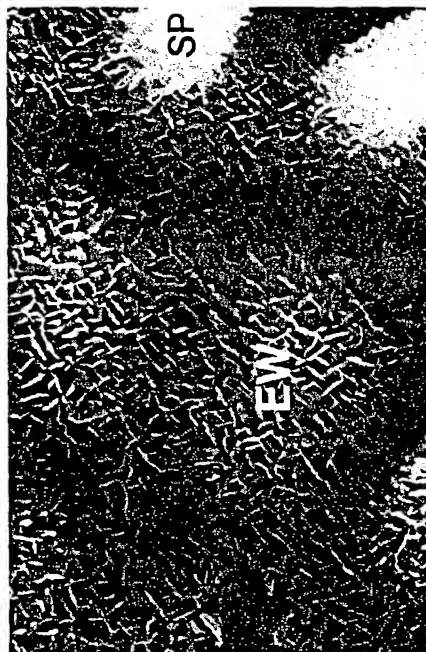
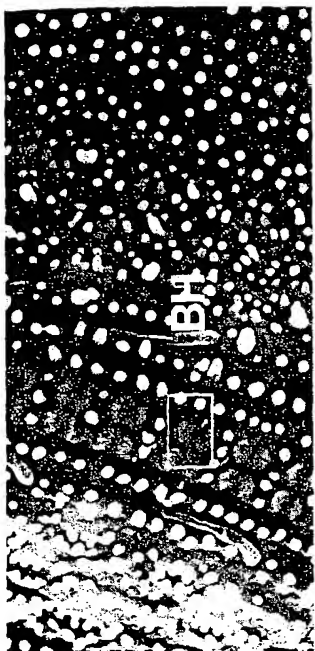
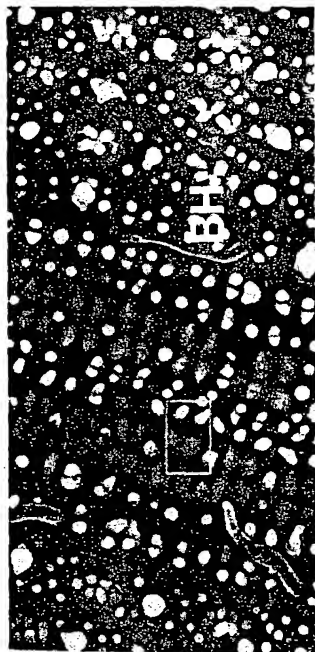




M101 (Glabrous, Japonica)  
5000X

500X

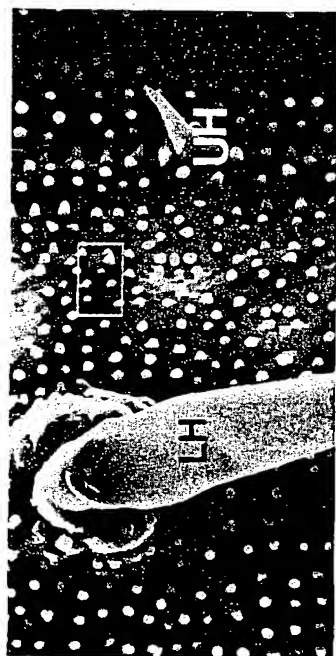
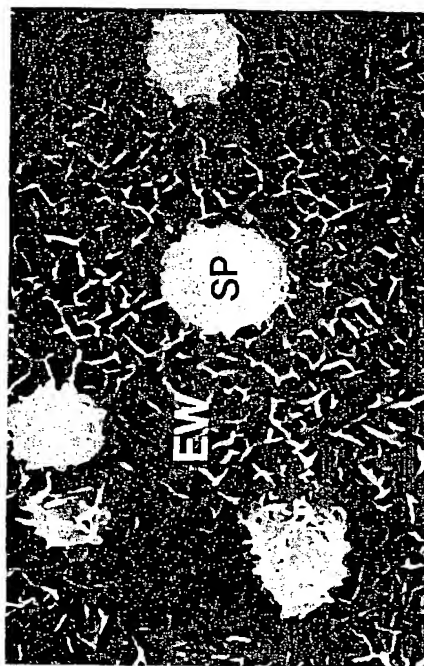




Adaxial

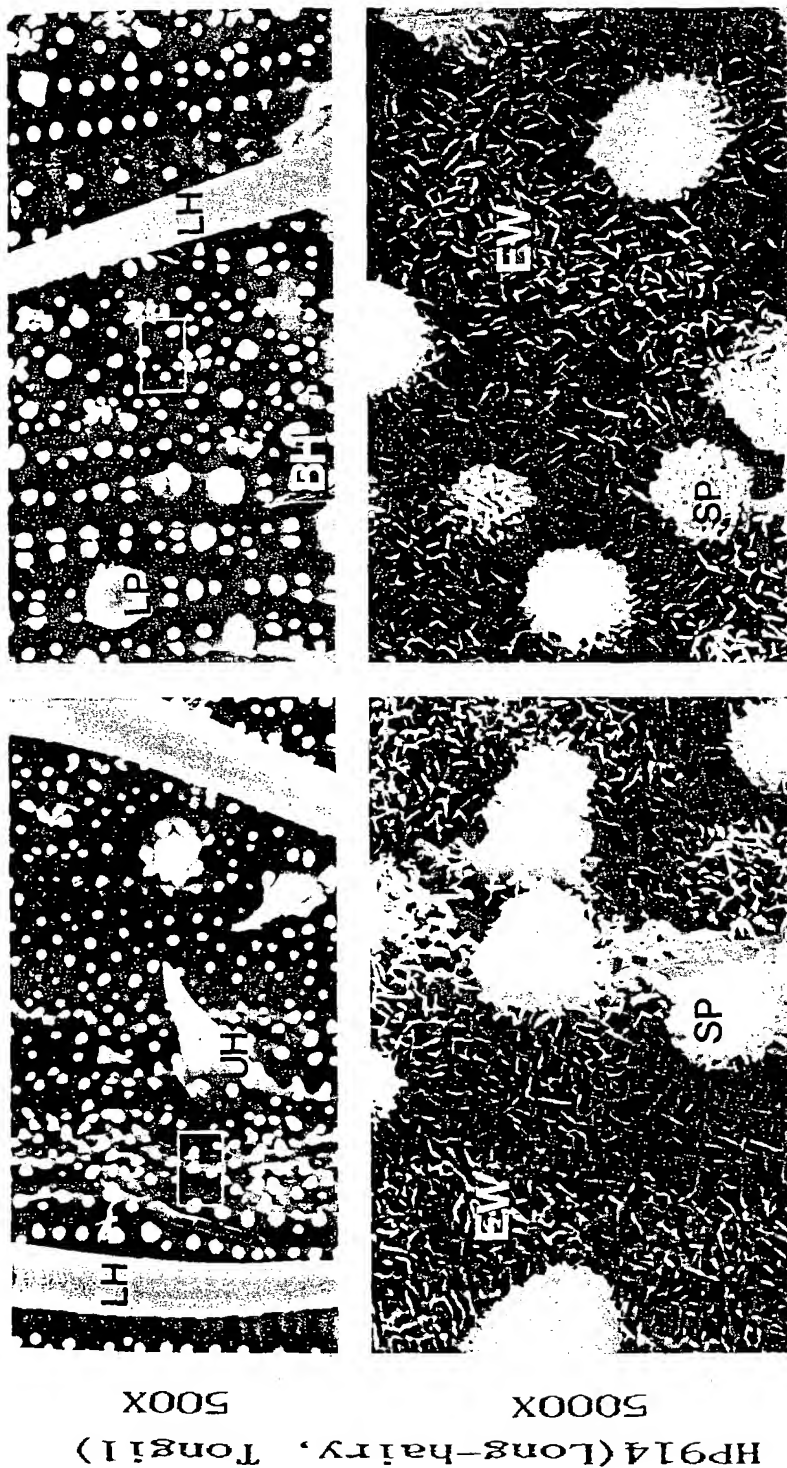
Abaxial

FIGURE 1. SEM photographs of glabrous rice leaf surfaces (flag leaf, varieties M101 and wx817). The lower part of the photographs represents a 10x magnification of the region marked by the white rectangular box. BH, bicellular microhair; EW, epicuticular wax; S, stomata; SP, small papillae.



LK2-7 (Long-hairy, Japonica)  
5000X

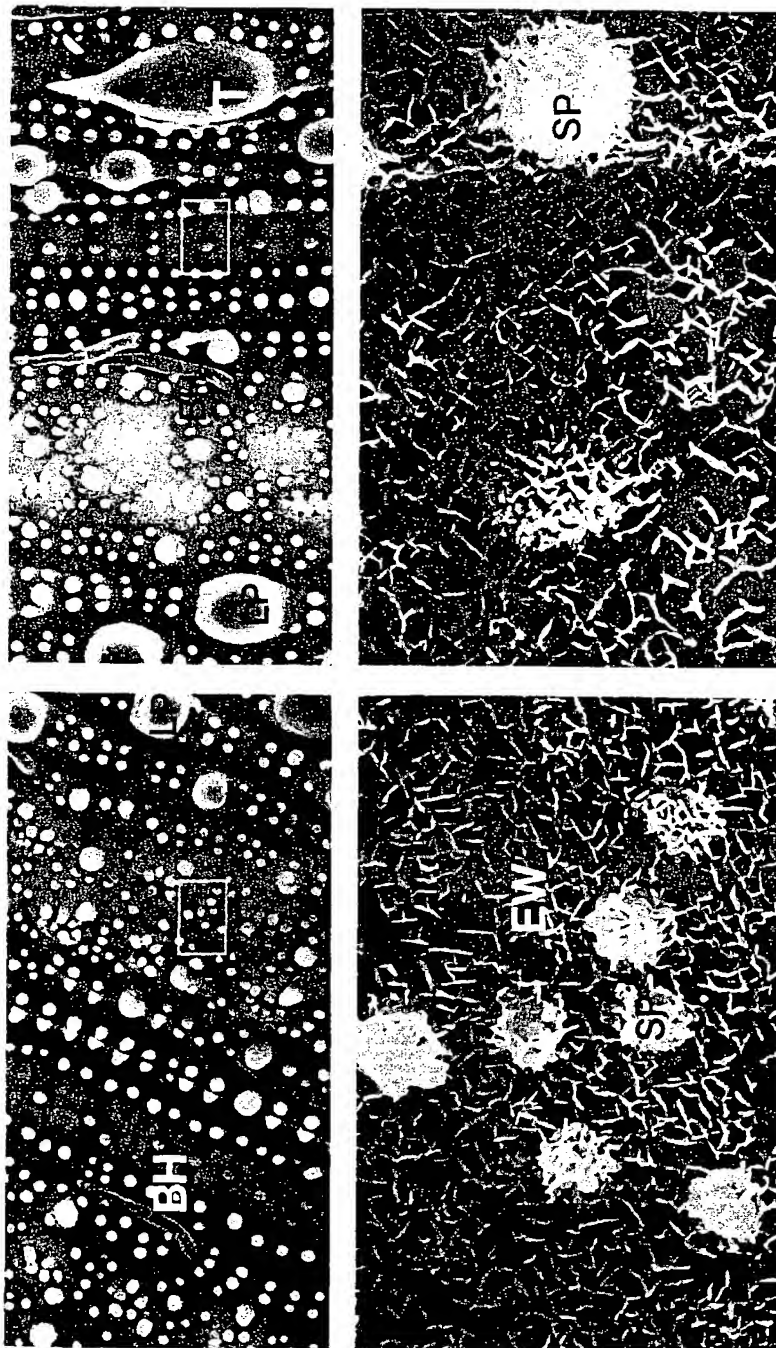
500X



Adaxial

Abaxial

FIGURE 2. SEM photographs of long hairy rice leaf surfaces (flag leaf, varieties LK2-7 and HP914). The lower part of the photographs represents a 10x magnification of the region marked by the white rectangular box. BH, bicellular microhair; LH, long hair; LP, large inflated papillae; SP, small papillae; EW, epicuticular wax; UH, unicellular microhair.

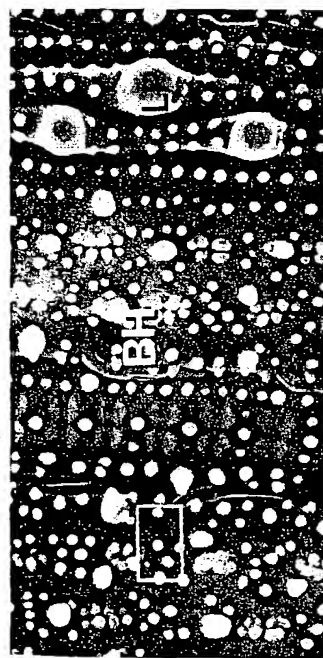
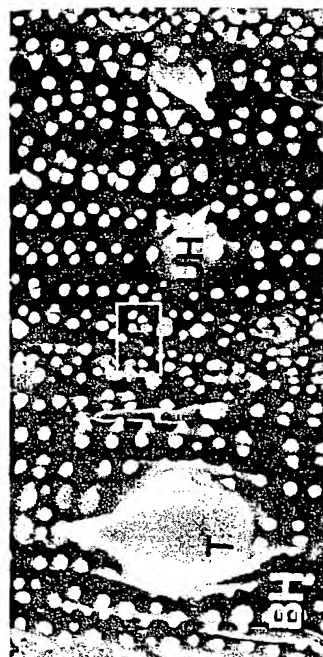


ChuCheong (Pubescent, Japonica)  
5000X

500X



# CheongCheong (Pubescent, Tongil)



500X



5000X

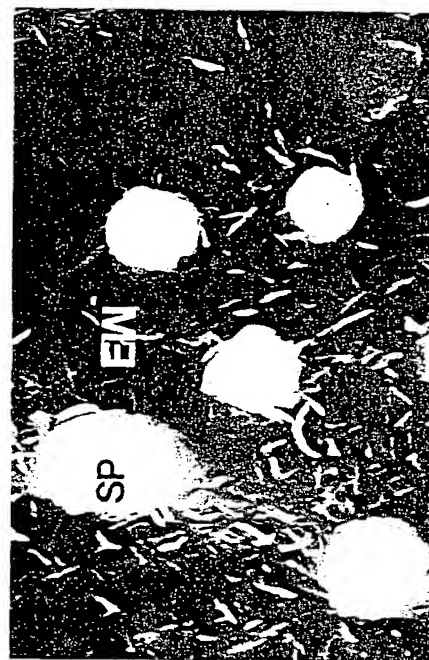
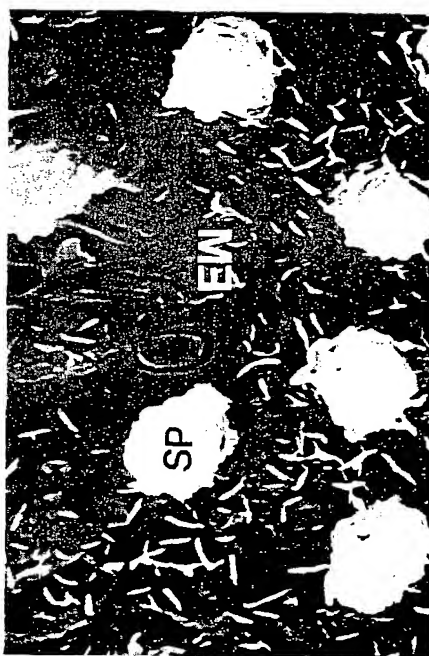
Abaxial

Adaxial

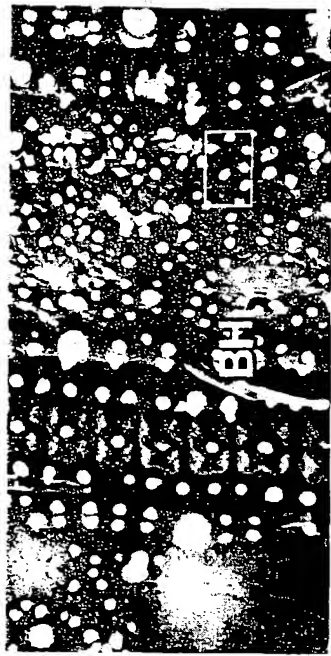
FIGURE 3. SEM photographs of pubescent rice leaf surfaces (Flag leaf, varieties Chucheong and Cheongcheong). The lower part of the photographs represents a 10X magnification of the region marked by the white rectangular box. BH, bicellular microhair; EW, epicuticular wax; SP, small papillae; LP, large inflated papillae; T, trichome; UH, unicellular microhair.

HP857 (water-wettable, Japonica)

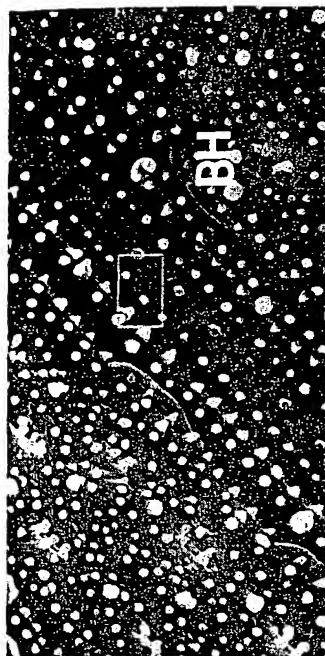
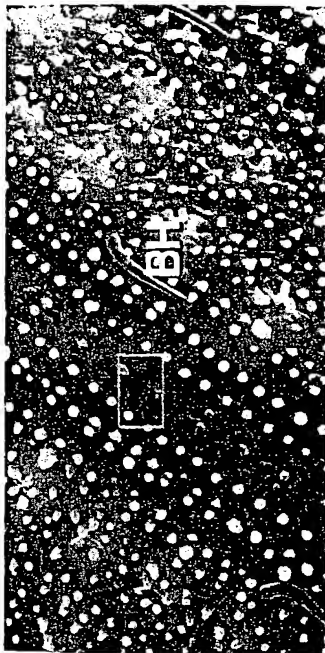
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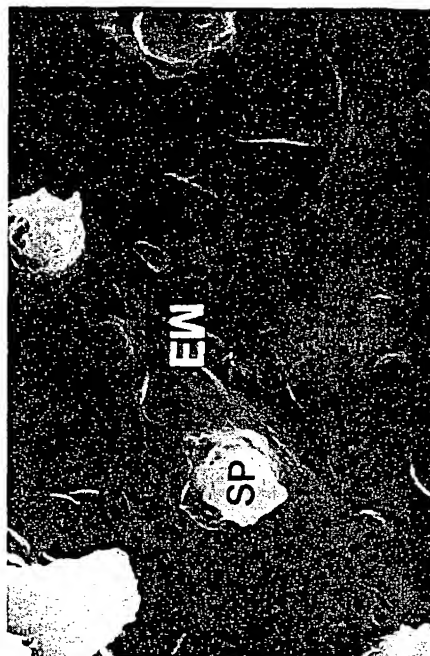
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wx139 (water-wettable, Tongil)  
500X



5000X



Adaxial

Abaxial

FIGURE 4. SEM photographs of water-wettable rice leaf surfaces (flag leaf, varieties HP857 and wx139). The lower part of the photographs represents a 10x magnification of the region marked by the white rectangular box. BH, bicellular microhair; EW, epicuticular wax; LP, large inflated papillae; SP, small papillae.



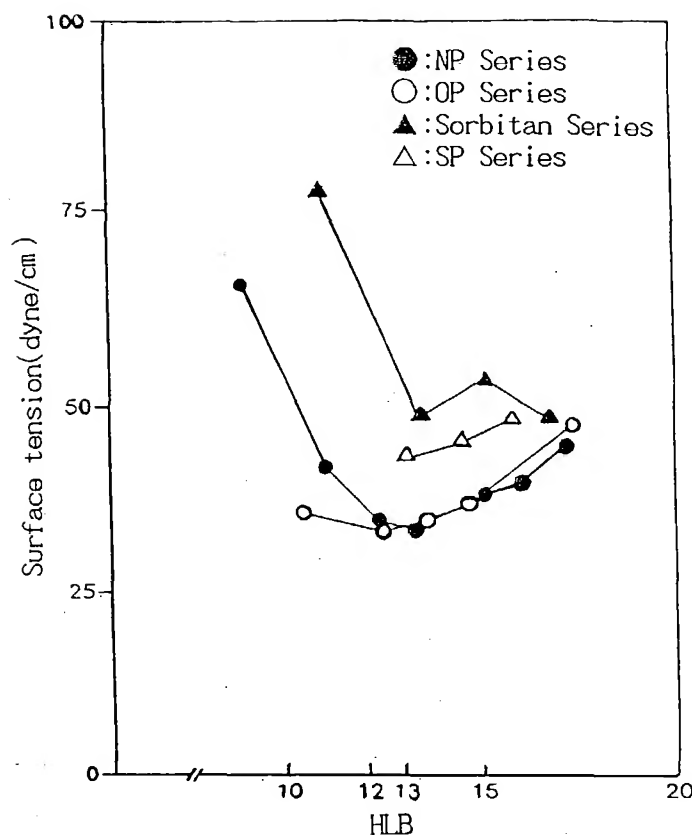


FIGURE 5. Relationship between surface tensions and HLB values among the nonionic surfactants used herein.

results suggest that adhesional force is a better criterion than contact angle for evaluating the wettability of nonionic surfactant solutions.

The contact angle increased more on the water-wettable than on the glabrous, long-hairy, and pubescent leaf surfaces, but the adhesional forces decreased less compared to the increase in the contact angle on the varieties of leaves (Figures 10 and 11). These results suggest that the wettability of intact leaf surfaces varies with the degree of wax coverage of the rice varieties rather than with differences in the fine morphology of the leaf surface (Figures 1 to 4).

Adhesional force had a significant relationship ( $r = 0.948^{**}$ ) with contact angle for the eight rice varieties tested (Figure 12). The results shown in Figures 10 and 11 indicate strongly that adhesional force is a better criterion than contact angle in evaluating the wettability of nonionic surfactant solutions.

In conclusion, for increased wettability of the rice leaf surface, the HLB values of useful surfactants should lie in the range of 12 to 13, the surface tension should be about 35 dyn/cm, and a surfactant belonging to the NP or OP group is recommended. As a single criterion for selecting a proper surfactant, adhesional force appears to be the best choice.

\*\* Highly significant statistically for the correlation  $r$ -value.

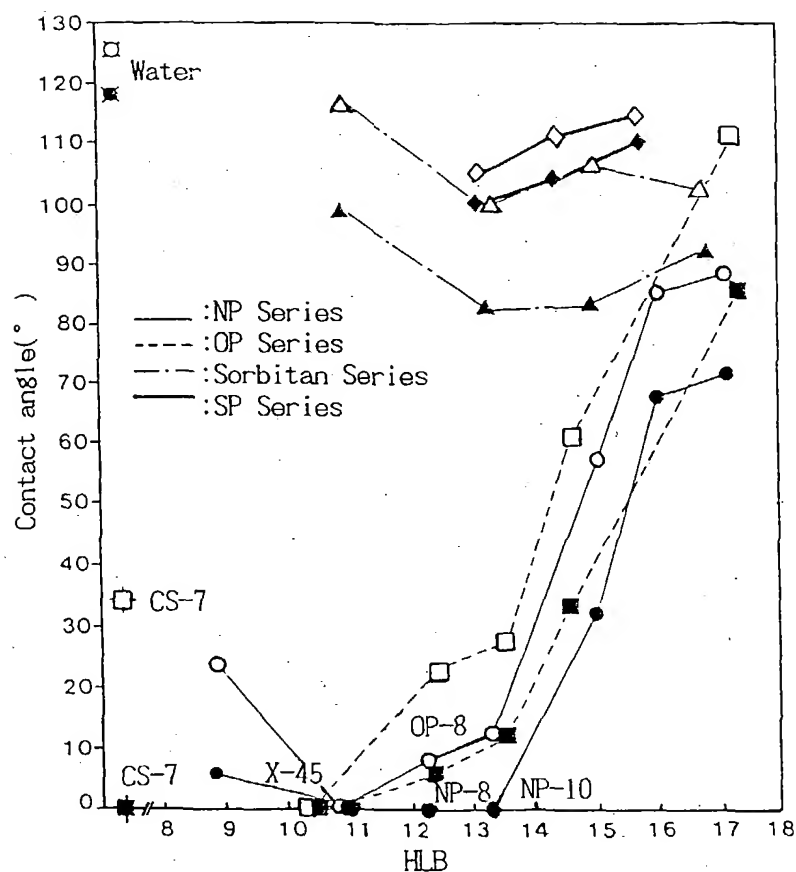


FIGURE 6. Relationship between HLB values of the nonionic surfactants and contact angles of 2- $\mu$ l surfactant droplets measured on intact leaf surfaces of eight rice varieties at two different stages.

- |                            |                              |
|----------------------------|------------------------------|
| ● NP series, heading       | ○ NP series, tillering       |
| ■ OP series, heading       | □ OP series, tillering       |
| ▲ Sorbitan series, heading | △ Sorbitan series, tillering |
| ◆ SP series, heading       | ◇ SP series, tillering       |
| ✱ Distilled water, heading | □ Distilled water, tillering |
| ✱ Triton CS-7, heading     | □ Triton CS-7, tillering     |

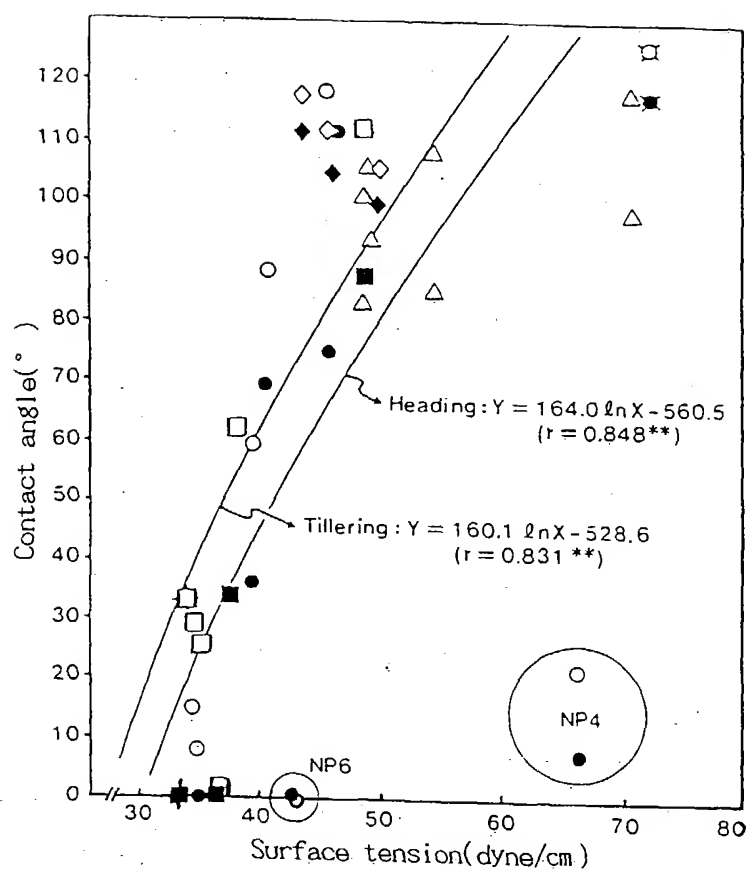


FIGURE 7. Relationship between surface tensions of 0.1% (w/v) nonionic surfactant solutions and contact angles measured on intact leaf surfaces of eight varieties at tillering and heading stages. NP-4 and NP-6 (denoted by a circle) have exceptionally low contact angles even though they have high surface tensions.

- |                            |                              |
|----------------------------|------------------------------|
| ● NP series, heading       | ○ NP series, tillering       |
| ■ OP series, heading       | □ OP series, tillering       |
| ▲ Sorbitan series, heading | △ Sorbitan series, tillering |
| ◆ SP series, heading       | ◇ SP series, tillering       |
| ■ Distilled water, heading | □ Distilled water, tillering |
| ■ Triton CS-7, heading     | □ Triton CS-7, tillering     |

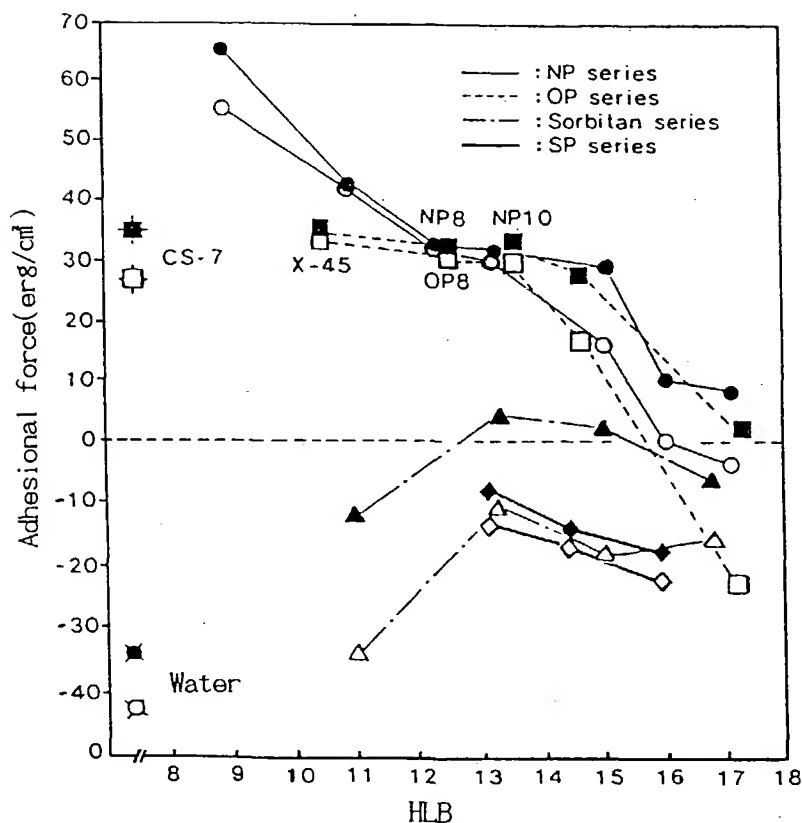


FIGURE 8. Relationship between HLB values of nonionic surfactants and adhesional forces of their 0.1% (w/v) water solutions on intact leaf surfaces of eight varieties at tillering and heading stages. Data are the average of adhesional forces ( $W_a = r_l \times \cos\theta$ ) calculated by measured contact angles ( $\theta$ ) and surface tensions ( $r_l$ ) on intact leaf surfaces of eight rice varieties.

- |                            |                              |
|----------------------------|------------------------------|
| ● NP series, heading       | ○ NP series, tillering       |
| ■ OP series, heading       | □ OP series, tillering       |
| ▲ Sorbitan series, heading | △ Sorbitan series, tillering |
| ◆ SP series, heading       | ◇ SP series, tillering       |
| ✱ Distilled water, heading | ✱ Distilled water, tillering |
| ✱ Triton CS-7, heading     | ✱ Triton CS-7, tillering     |

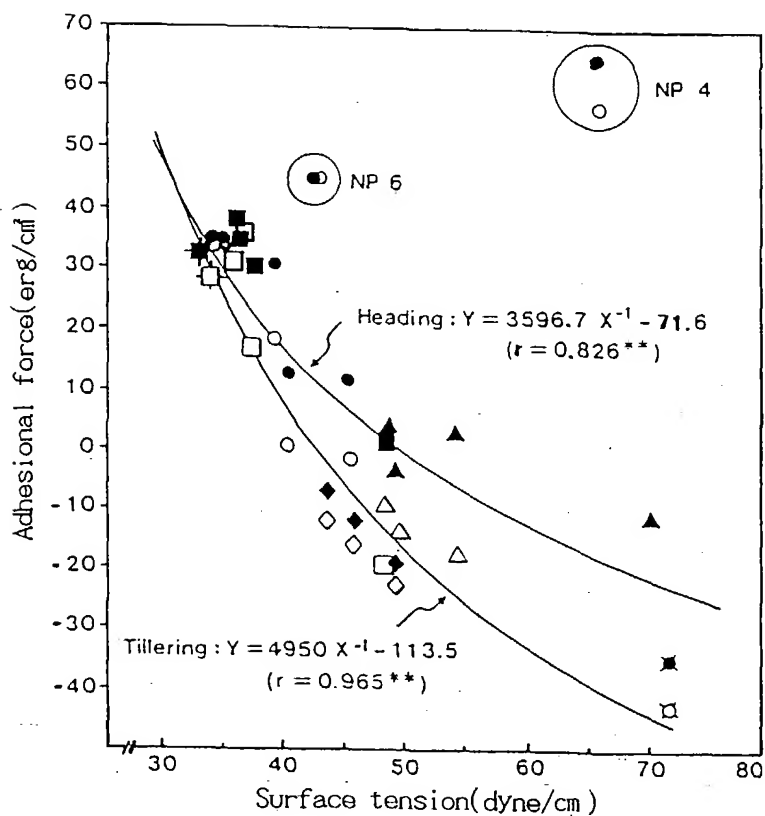
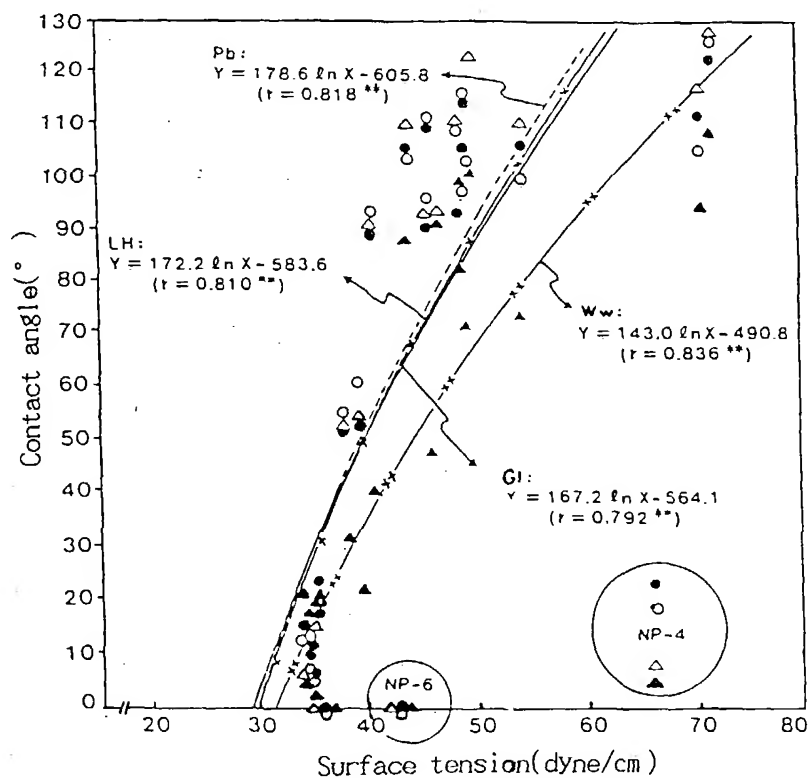


FIGURE 9. Relationship between surface tensions of 0.1% (w/v) nonionic surfactant solutions and the average adhesional forces calculated by their surface tension and cosine values of contact angles on intact leaf surfaces of eight varieties at tillering and heading stages. NP-4 and NP-6 (denoted by a circle) have exceptionally high adhesional forces even though they have high surface tensions.

- |                            |                              |
|----------------------------|------------------------------|
| ● NP series, heading       | ○ NP series, tillering       |
| ■ OP series, heading       | □ OP series, tillering       |
| ▲ Sorbitan series, heading | △ Sorbitan series, tillering |
| ◆ SP series, heading       | ◇ SP series, tillering       |
| ✱ Distilled water, heading | ✱ Distilled water, tillering |
| ✱ Triton CS-7, heading     | ✱ Triton CS-7, tillering     |



**FIGURE 10.** Relationship between surface tensions of 0.1% (w/v) nonionic surfactant solutions and contact angles on rice leaf surfaces among rice varieties classified by leaf surface property. Data are the averages of 2- $\mu$ l surfactant droplets measured on intact leaf surfaces. NP-4 and NP-6 (denoted by a circle) have exceptionally low contact angles even though they have high surface tensions.

- Glabrous (G)
- Long-hairy (LH)
- ▲ Pubescent (Pb)
- △ Water wettable (Ww)

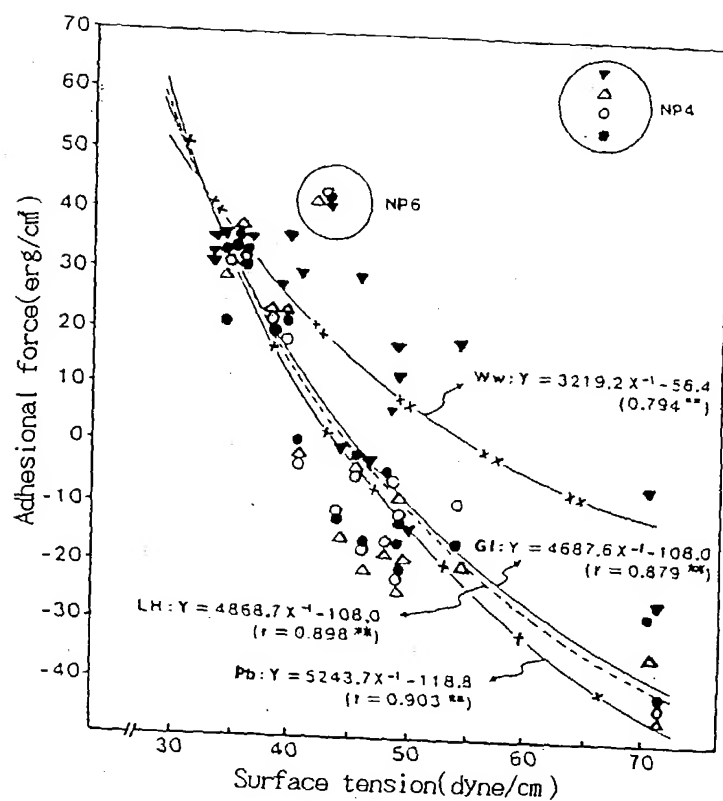


FIGURE 11. Relationship between surface tensions of 0.1% (w/v) nonionic surfactant solutions and adhesion forces on rice leaf surfaces among rice varieties classified by leaf surface property. Data are the averages of adhesion forces calculated by surface tensions of surfactant solutions and their contact angles on intact leaf surfaces. NP-4 and NP-6 (denoted by circle) have exceptionally high adhesion forces even though they have high surface tensions.

- Glabrous (GI)
- Long-hairy (LH)
- △ Pubescent (Pb)
- ▼ Water wettable (Ww)



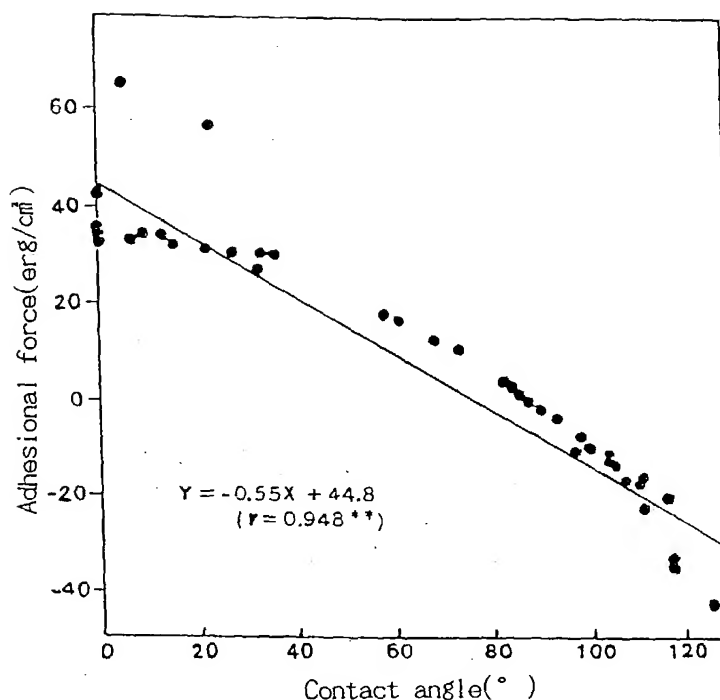


FIGURE 12. Relationship between contact angles on intact leaf surfaces and adhesional forces calculated by surface tensions of 0.1% (w/v) nonionic surfactant solutions and their contact angles on intact rice leaf surfaces. Data are the averages for the eight rice varieties.

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## Chapter 4

**SURFACTANT-INDUCED ETHYLENE EVOLUTION AND  
PIGMENT EFFLUX FROM BEET (*BETA VULGARIS* L.) ROOT  
TISSUE**

Hiroyuki Matsui, Warren E. Shafer, and Martin J. Bukovac

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## ABSTRACT

The physiological activity of selected surfactants commonly used in agriculture and/or representing selected chemistries was determined using beet root tissue (*Beta vulgaris* L.) as a model system. Biological activity was assessed by measuring simultaneously the effect of the surfactant on the induction of ethylene evolution and on membrane integrity. Tissue discs were incubated in appropriate test solutions at pH 7 for 3 h at 30°C in the dark. Ethylene was determined by gas chromatographic analysis of headspace samples, and membrane integrity was assessed by spectrophotometrically measuring betacyanin efflux into the incubation medium. Surfactants either promoted, had no effect on, or suppressed ethylene evolution, while they either increased or had no effect on membrane permeability. Responses of both systems were related to surfactant chemistry and concentration. Of 29 surfactants evaluated, 18 enhanced both ethylene evolution and betacyanin efflux, while only 5 enhanced ethylene production without affecting membrane integrity. Five enhanced betacyanin efflux but depressed ethylene evolution. One had no significant effect on either parameter. In general, polyoxyethylene derivatives of octylphenol, nonylphenol, and linear alcohols (C<sub>9</sub>, C<sub>11</sub>, C<sub>12-15</sub> hydrophobe) decreased in biological activity with increasing oxyethylene chain length. For most surfactants, the minimum effective concentrations for induction of ethylene evolution and pigment efflux were 0.01 and 0.05%, respectively. The relationships between surfactant chemistry and ethylene evolution and membrane integrity are discussed.

## I. INTRODUCTION

Surfactants are commonly used in agrichemical formulations to stabilize emulsions and/or suspensions,<sup>4</sup> increase retention and spreading of spray droplets,<sup>12,13</sup> and enhance penetration of the active ingredient.<sup>12</sup> Unfortunately, many surfactants possess biological activity in plant systems,<sup>34</sup> including inhibition of root,<sup>15,17,35</sup> coleoptile,<sup>47</sup> callus,<sup>10</sup> suspension cultures,<sup>7</sup> and frond growth/development,<sup>6</sup> inhibition of seed germination,<sup>18</sup> and the induction of cellular necrosis and subsequent tissue collapse in leaf organs.<sup>21-23</sup> While several mechanisms of surfactant action in plant tissues have been identified, the most common appears to be disruption of membrane integrity.<sup>3,8,11,16,30,44</sup> In fact, surfactants are frequently used to solubilize the lipid:protein components of membranes.<sup>16</sup> In light of this, considerable effort has focused on quantifying the impact of surfactants on membrane integrity. The most commonly used method to quantify the disruption of membrane integrity has been to measure pigment and/or ion efflux.<sup>5,29,32,40,41,45</sup> Surfactant-enhanced ethylene production is also a membrane-related phenomenon.

Lownds and Bukovac<sup>23</sup> and Stevens and Bukovac<sup>43</sup> studied the induction of ethylene evolution in leaf tissue by surfactants and reported that ethylene evolution was inversely related to polyoxyethylene (POE) chain length for a series of nonionic (octylphenol derivatives) surfactants. Numerous investigators<sup>5,29,32,45</sup> have utilized betacyanin efflux from beet root tissue to assess the toxicity of selected nonionic, anionic, and cationic surfactants. In general, toxicity was related to surfactant chemistry (ionic surfactants were typically more toxic than nonionic surfactants), concentration (toxicity increased with increasing concentration), and in the case of POE surfactants, POE content (toxicity was inversely related to POE chain length).

Based on the data presented in the preceding text, it is clear that the need to incorporate a surfactant(s) in an agrichemical formulation/spray solution should be balanced against the possible deleterious biological activity of the surfactant(s) in plant systems. To realistically achieve this goal, a basic understanding of surfactant chemistry/biological activity relationships must be obtained. In addition, a relatively simple bioassay system should be available

so that a candidate surfactant can be rapidly tested for possible adverse responses in plant tissues.

The beet root disc assay offers two important advantages over the leaf/ethylene assays mentioned above, namely, rapidity (a few hours to complete vs. a few days) and the absence of a cuticular barrier to uptake/penetration. With respect to the latter point, although there is mounting evidence that surfactants penetrate foliage/plant cuticles,<sup>36,42,43</sup> it is important to distinguish between differences in penetration and differences in innate biological activity.

Given the profound effects of surfactants on both ethylene production and pigment efflux in plant tissues, as well as the advantages of the beet root disc assay, we were interested in determining whether both responses could be studied simultaneously using beet root tissue. Once the assay system was optimized, we evaluated a number of commercially important surfactants, varying in chemistry, to probe surfactant chemistry/biological activity relationships. The results of our studies are reported herein.

## II. MATERIALS AND METHODS

### A. PLANT MATERIAL/TISSUE PREPARATION

Fresh beets (*Beta vulgaris* L.) were purchased locally. After removing the apical and basal portions (each about 25% of the total root), 6-mm diameter cylinders were removed longitudinally from between the vascular rings of the median segment using a cork borer. The excised cylinder was then sectioned transversely into 2-mm-thick discs using a hand microtome. Only discs free of visual defects or distortion were used.

### B. ASSAY PROCEDURE

Twenty discs were placed on filter paper in 25-ml Erlenmeyer flasks containing 1 ml of treatment solution. The 1-ml solution volume was selected because adequate tissue exposure was obtained without the risk of the discs floating/bumping together or being submerged. Six replicate flasks were used per treatment. The flasks were immediately sealed with rubber septa and incubated in the dark. The specific assay conditions are described below (see Section II.C).

Ethylene was measured in a 1-ml headspace gas sample by gas chromatography.<sup>23</sup> Betacyanin efflux into the treatment (incubation) solution was quantified by removing the discs from each flask, adding 9 ml of 1% HCl:methanol, and then reading the absorbance at 540 nm with a spectrophotometer (Bausch & Lomb, Model 20).

Due to root to root variability in betacyanin content, absolute absorbance data from a set of discs could not be used to quantify surfactant effects. Instead, 120 representative discs were selected from the total sample pool immediately prior to initiating each experiment and divided into six replicates of 20 discs each. Each replicate was exhaustively extracted with 50 ml of 1% HCl:methanol and the absorbance (540 nm) measured. The percentage of betacyanin efflux induced by the respective treatment was then calculated according to:

$$\% \text{ betacyanin efflux} = \frac{\text{amount betacyanin in incubation medium}}{\text{amount betacyanin extracted from discs}} \times 100 \quad (1)$$

### C. ASSAY DEVELOPMENT/OPTIMIZATION

Ethylene production and pigment efflux were optimized to ensure that treatment responses could be quantified. Several experimental parameters of critical importance to our assay were examined. These included ethylene substrate (1-aminocyclopropane-1-carboxylic acid, ACC; Calbiochem) concentration, disc-rinsing time, buffer pH, incubation temperature, incubation time-course, and buffer composition. Given the large number of variables and

our interest in sequentially investigating each individually, it was necessary to arbitrarily set certain test conditions until the optimal condition was established in the appropriate range-finding study.

### 1. Effect of Ortho X-77 Concentration

Due to the marked effect surfactants have on solution properties and the possibility that such changes might influence the results obtained during our method-development experiments, Ortho X-77 (Table 1) was selected as the standard surfactant for optimization of our assay. Three concentrations (0.01, 0.1, and 1.0% w/v) were examined to establish the effect of concentration on ethylene evolution and pigment efflux. The assay conditions were: disc rinse period, 15 h; 100 mM phosphate buffer, pH 6.7; temperature, 25°C; incubation time, 3 h. Ethylene evolution increased approximately 2.5-fold between controls (no Ortho X-77) and the 1.0% treatment (data not shown). There was no pigment efflux from controls or the 0.01% Ortho X-77 treatment. However, pigment efflux increased from 4 to 13% as the Ortho X-77 concentration was increased from 0.1 to 1.0%. Based on these data, we selected 1.0% Ortho X-77 as a standard concentration to establish the remaining parameters.

### 2. Effect of Disc-Rinsing Time

Rinsing the root discs with distilled water (20°C) was necessary to remove pigment remaining on the cut surfaces which could interfere with data interpretation. Sets of discs were rinsed for selected periods of time (3 to 15 h, at 3-h intervals) and then incubated. The assay conditions were: 100 mM phosphate buffer, pH 6.7; temperature, 25°C; incubation time, 3 h. Ethylene production increased linearly as rinse times were increased to 9 h, but then decreased slightly as rinse times were increased to 15 h (data not shown). Pigment efflux decreased slightly with an increase in rinse times. Based on these data and scheduling convenience, we selected 10 to 11 h as our routine disc rinse period.

### 3. Effect of ACC Concentration

ACC is the primary substrate for ethylene biosynthesis in plant tissue.<sup>48,49</sup> Due to concerns about the depletion of endogenous ACC during disc rinsing, we evaluated the need to supply ACC (10  $\mu$ M to 100 mM) in the treatment solution. The assay conditions were: disc rinse period, 11 h; 100 mM phosphate buffer, pH 7.0; temperature, 25°C; incubation time, 3 h. Ethylene evolution increased with increasing ACC concentration, reaching a maximum at 10 mM (Figure 1A). ACC did not induce pigment efflux. When combined with 1.0% Ortho X-77, ethylene production was greater for all ACC concentrations examined, with maximal production still at 10 mM. ACC had no significant effect on the amount of pigment efflux induced by Ortho X-77. Based on these data, 10 mM ACC was routinely included in the remaining assays.

### 4. Effect of Buffer pH

The effect of pH was examined over the range of 3 to 9 using 100 mM phosphate buffer. The assay conditions were: disc rinse period, 11 h; Ortho X-77 concentration, 1.0%; ACC concentration, 10 mM; temperature 25°C; incubation time, 3 h. Ethylene production increased linearly from pH 3 to 7 and then declined at pH 8 and 9 (Figure 1B). Pigment efflux followed a similar pattern. Thus, buffer pH was routinely set at 7.0.

### 5. Effect of Temperature

Temperature effects, during incubation, on ethylene production and pigment efflux were tested over the range of 20 to 40°C. The assay conditions were: disc rinse period, 10 h; 100 mM phosphate buffer, pH 7.0; Ortho X-77 concentration, 1.0%; ACC concentration, 10



TABLE 1  
Selected Chemical Characteristics of Surfactants Examined<sup>a</sup>

Trade name	Code #	Source <sup>b</sup>	POE <sup>c,d</sup>	MW <sup>d</sup>	HLB	cmc (%)
Representative Nonionic Surfactants						
Ortho X-77	1	3	NA <sup>e</sup>	NA	NA	0.01
Triton X-100	2	6	9.5	628	13.5	0.019
Triton X-405	3	6	40.0	1966	17.9	0.17
Tween 20	4	5	20.0	1244	16.7	0.006
Tween 80	5	5	20.0	1370 <sup>f</sup>	15.0	0.004 <sup>g</sup>
Representative Anionic Surfactants						
Duponol	6	4	NA	288	NA	0.24
Aerosol OT	7	1	NA	444	NA	0.03
Aerosol OT-B	8	1	NA	444	NA	0.03 <sup>h</sup>
Representative Cationic Surfactants						
Arquad 2C-75	9	2	NA	447	NA	0.01
Arquad C-50	10	2	NA	278	NA	0.009
Nonionic Surfactant Series						
Neodol 91 Series		7				
91-6	11		6.0	425	12.4	0.025
91-8	12		8.0	529	14.0	0.027
91-10	13		10.0	600	14.7	0.029
91-12	14		12.0	680	15.3	0.031
91-20	15		20.0	1040	16.9	0.039
Neodol 25 Series		7				
25-3	16		3.0	336	7.9	0.0001
25-7	17		7.0	522	12.2	0.0009
25-9	18		9.0	610	13.3	0.0018
25-12	19		12.0	729	14.4	0.0027
25-30	20		30.0	1548	17.1	0.016
Triton X Series		6				
X-15	21		1.0	250	3.6	0.001
X-35	22		3.0	338	7.8	0.004
X-45	23		5.0	426	10.4	0.005
X-114	24		7.5	536	12.4	0.009
X-102	25		12.5	756	14.6	0.029
X-305	26		30.0	1526	17.3	0.11
Triton N Series		6				
N-42	27		4.0	405	9.1	0.0021 <sup>i</sup>
N-57	28		5.0	440	10.0	0.0025
N-150	29		15.0	880	15.0	0.0083

<sup>a</sup> Data from References 21, 31, and 43.

<sup>b</sup> Source codes: 1 = American Cyanamid, Wayne, NJ; 2 = Armac Co., Chicago, IL; 3 = Chevron Chemical Co., Richmond, CA; 4 = E. I. du Pont de Nemours & Co., Wilmington, DE; 5 = ICI Americas, Inc., Wilmington, DE; 6 = Rohm & Haas, Philadelphia, PA; 7 = Shell Oil Co., Houston, TX.

<sup>c</sup> Polyoxyethylene content.

<sup>d</sup> Average values.

<sup>e</sup> Either not applicable or not available.

<sup>f</sup> Personal communication, M. Patel (ICI Americas, Inc., Wilmington, DE).

<sup>g</sup> Unpublished data. A. Heredia (Michigan State University, East Lansing).

<sup>h</sup> The assumption was made that the presence of sodium benzoate in the Aerosol OT-B (the only difference between OT and OT-B) did not significantly affect the cmc.



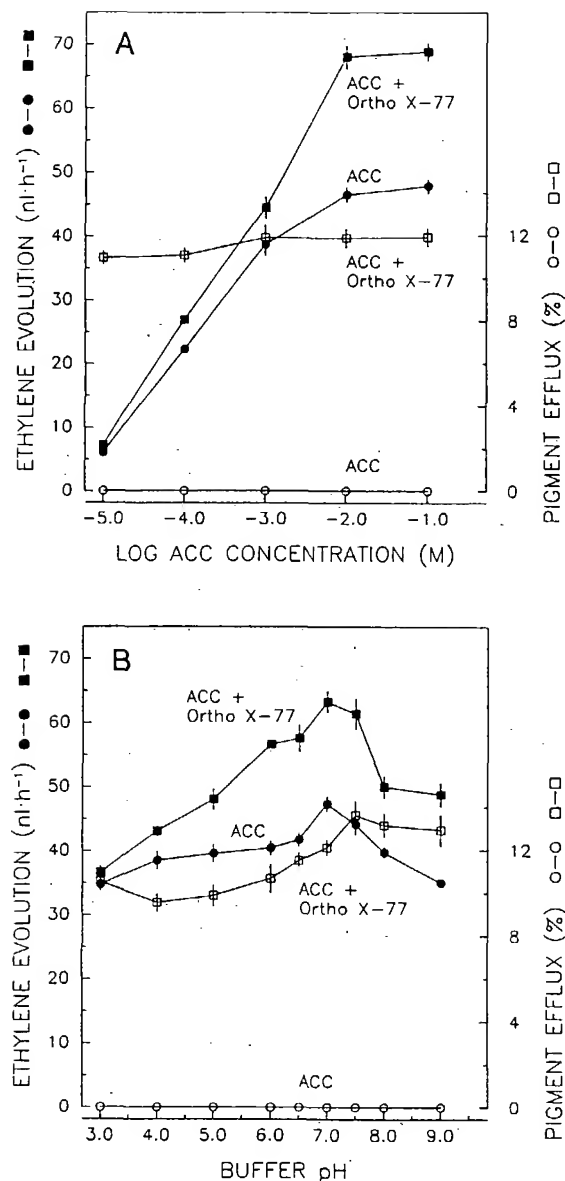


FIGURE 1. Effect of ACC concentration (A) and pH of incubation medium (B) on ethylene evolution and pigment efflux from beet root tissue. See text for specific assay conditions.

mM; incubation time, 3 h. Ethylene production resembled a bell-shaped curve, with a maximum at 30°C (Figure 2). Pigment efflux increased slightly between 20 and 30°C, but increased dramatically at 35 and 40°C. Therefore, 30°C was routinely adopted for all assays.

#### 6. Time Course of Ethylene Production and Pigment Efflux

Ethylene evolution and pigment efflux were monitored over a 24-h period to document time-dependent responses. Assay conditions were: disc rinse period, 10 h; 100 mM phosphate buffer, pH 7.0; Ortho X-77 concentration, 1.0%; ACC concentration, 10 mM; temperature,

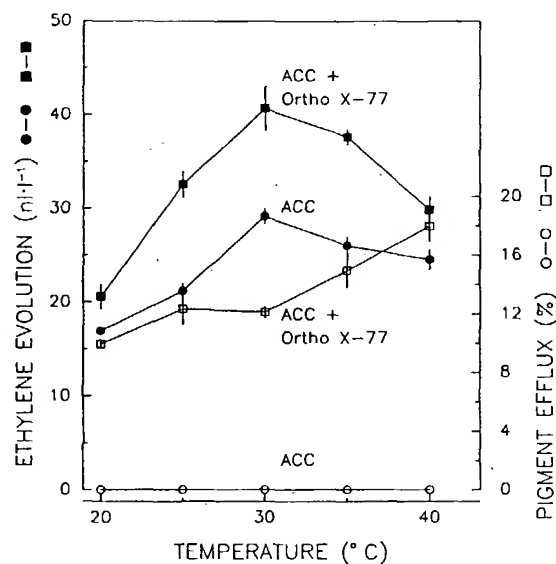


FIGURE 2. Effect of assay temperature on ethylene evolution and pigment efflux from beet root tissue. See text for specific assay conditions.

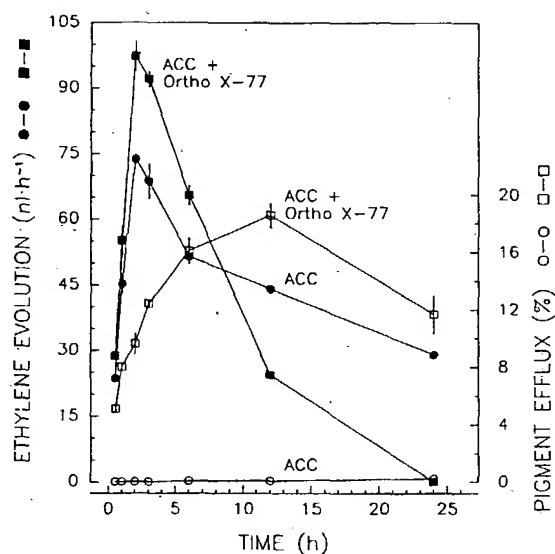


FIGURE 3. Time course of ethylene evolution and pigment efflux from beet root tissue. See text for specific assay conditions.

30°C; incubation time, 3 h. Initially, ethylene levels increased sharply, reaching a maximum at 2 h (Figure 3). Thereafter, ethylene production decreased steadily and approached background levels after 24 h. Pigment efflux also increased sharply at first, reaching a maximum at 12 h, and then decreased after 24 h. Based on these data and scheduling convenience, we selected 3 h as our standard assay period. While this time interval was not optimum for pigment efflux, sufficient efflux of pigment occurred by 3 h for quantification.

TABLE 2  
Effect of Hydrophobe for Two Alkyl (12EO) and Two Aryl (5EO) Surfactants on  
Ethylene Evolution (% of Control)

Hydrophobe	Concentration (%)					
	0.01	0.05	0.1	0.5	1.0	2.0
C <sub>9-11</sub> linear alcohol <sup>a</sup> (Neodol 91-12)	99 (5) <sup>b</sup>	158 (3)	144 (5)	118 (3)	106 (4)	ND <sup>c</sup>
C <sub>12-15</sub> linear alcohol <sup>a</sup> (Neodol 25-12)	119 (4)	ND	133 (5)	149 (3)	145 (6)	125 (4)
Octylphenol (Triton X-45)	127 (5)	140 (8)	130 (4)	108 (8)	104 (4)	ND
Nonylphenol (Triton N-57)	148 (4)	155 (4)	157 (6)	145 (4)	138 (7)	ND

<sup>a</sup> Mixture of hydrophobe chain lengths (C<sub>9-11</sub>, C<sub>12-15</sub>).

<sup>b</sup> Mean (SE).

<sup>c</sup> Not determined.

### 7. Buffer Composition

Four buffers (Tris, borate, citrate, and phosphate) were tested at 100 mM and pH 7.0. The assay conditions were: disc rinse period, 10 h; Ortho X-77 concentration, 1.0%; ACC concentration, 10 mM; temperature, 30°C; incubation time, 3 h. Both Tris and borate buffers yielded significantly greater amounts of ethylene than phosphate and citrate (data not shown). Pigment efflux induced in the Tris and borate buffer treatments was significantly lower than with the citrate and phosphate buffers. Since phosphate buffer represented an intermediate response for both parameters, it was selected for our assay.

### 8. Method Development/Optimization Summary

Based on these experiments, the following standard assay system was adopted for the surfactant studies: discs were rinsed (distilled water, 20°C) for 10 h prior to use and incubated (in the dark) at 30°C for 3 h with 10 mM ACC in 100 mM phosphate buffer at pH 7.0.

### D. SURFACTANTS

The surfactants utilized herein were obtained from commercial sources (Table 1). Trade names and general chemistries (in parentheses) for the surfactants/surfactant series used herein are Ortho X-77 (mixture of alkyaryl glycols, free fatty acids, and isopropanol), Triton X series (polyoxyethylene derivatives of octylphenol), Triton N series (polyoxyethylene derivatives of nonylphenol), Tween 20 (polyoxyethylene [20] sorbitan monolaurate), Tween 80 (polyoxyethylene [20] sorbitan monooleate), Duponol (sodium lauryl sulfate), Aerosol OT/Aerosol OT-B (dioctyl sodium sulfosuccinate; Aerosol OT-B is the same as Aerosol OT except that it contains sodium benzoate), Arquad 2C-75 (dicoco dimethyl ammonium chloride), Arquad C-50 (monococo trimethyl ammonium chloride), Neodol 91 series (polyethoxylated C<sub>9-11</sub> linear primary alcohol derivatives), and Neodol 25 series (polyethoxylated C<sub>12-15</sub> linear primary alcohol derivatives). All polyethoxylated surfactants (Table 1, POE column) were mixtures of ethoxymers, with the mole distribution following a Poisson distribution.<sup>39,46</sup> Also, for the Neodol linear alcohol series, the hydrophobe length ranged from C<sub>9-11</sub> or C<sub>12-15</sub>. No attempt was made to further purify the surfactants prior to use. Corrections were made for percent a.i. differences when necessary. All solution concentrations were based on weight/volume.

### E. DATA PRESENTATION

The data in Tables 2 and 3 and Figures 1 through 6 are means of six replicates (20 discs/replicate) with their respective standard error (SE) values. In the figures where SE

TABLE 3  
Effect of Hydrophobe for Two Alkyl (12EO) and Two Aryl (5EO) Surfactants on  
Pigment Efflux (%)

Hydrophobe	Concentration (%)					
	0.01	0.05	0.1	0.5	1.0	2.0
C <sub>9-11</sub> linear alcohol <sup>a</sup> (Neodol 91-12)	0 <sup>b</sup>	0	0.4 (<0.1) <sup>b</sup>	7.6 (0.5)	16.4 (0.7)	ND <sup>c</sup>
C <sub>12-15</sub> linear alcohol <sup>a</sup> (Neodol 25-12)	0	ND	0.7 (0.1)	1.0 (<0.1)	3.3 (0.1)	7.2 (0.4)
Octylphenol (Triton X-45)	0.2 (<0.1)	3.3 (0.3)	8.7 (0.6)	11.9 (0.7)	16.3 (0.7)	ND
Nonylphenol (Triton N-57)	0.2 (<0.1)	1.6 (0.1)	2.8 (0.2)	5.9 (0.4)	8.5 (0.5)	ND

<sup>a</sup> Mixture of hydrophobe chain lengths (C<sub>9-11</sub>, C<sub>12-15</sub>).

<sup>b</sup> Mean (SE).

<sup>c</sup> Not determined.

values are not shown, they were smaller than the data symbol. Ethylene data are presented as either the amount of ethylene evolved (nl/h; Figures 1 to 3) or as a percentage of the average amount of ethylene produced by control (i.e., no surfactant) discs (Figures 4 to 6). Betacyanin efflux data are presented as percent values (see Equation 1).

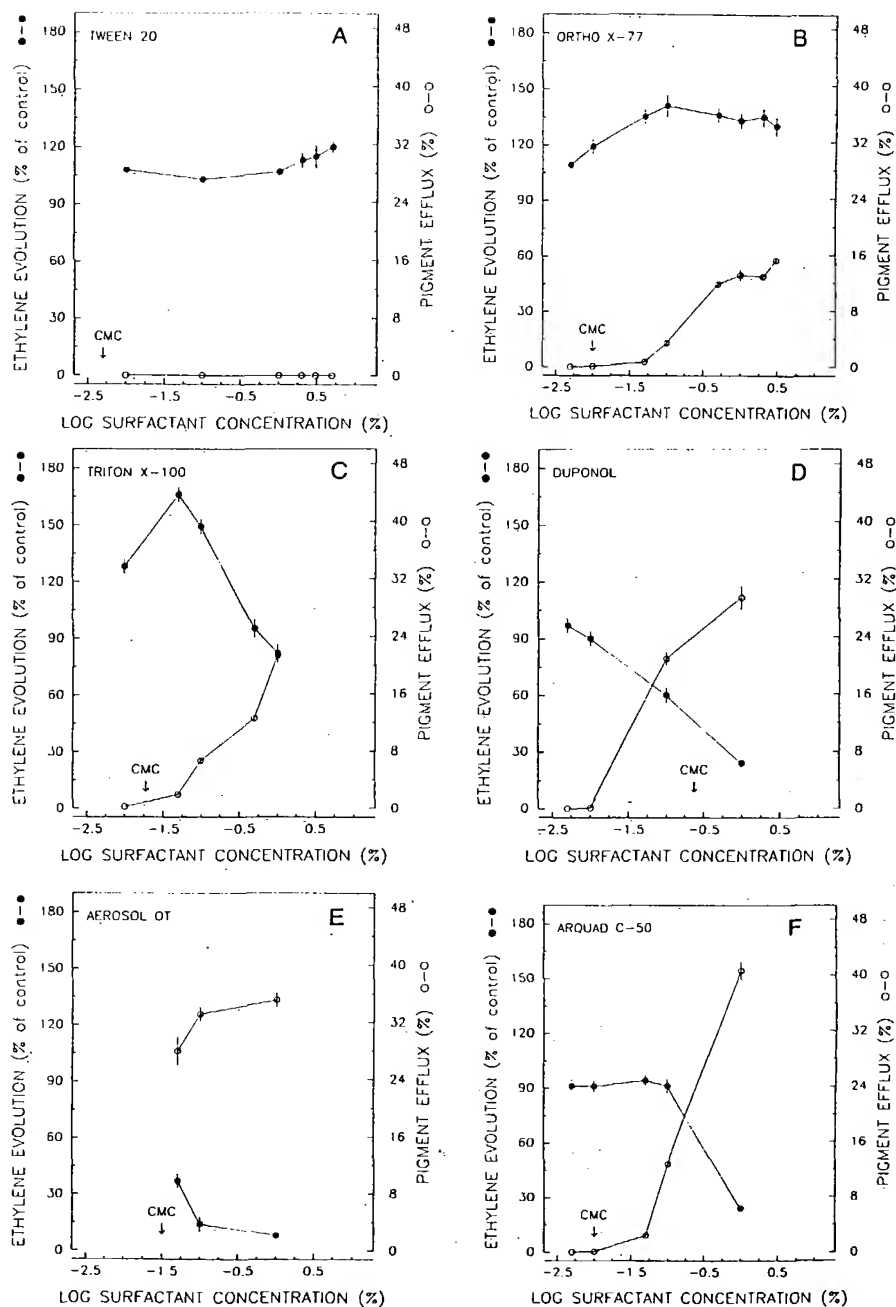
### III. RESULTS AND DISCUSSION

Two primary goals were established for these studies, namely: (1) optimize a bioassay system which would be useful for screening candidate surfactants for possible deleterious biological activity and (2) investigate surfactant chemistry/biological activity relationships for a selection of commonly used surfactants. While these goals have also been the focus of others,<sup>6,7,35,41</sup> including studies specifically utilizing beet root tissue,<sup>5,29,32,45</sup> our studies are unique because they stressed the effects of surfactants on two membrane-associated phenomena in the same plant system.

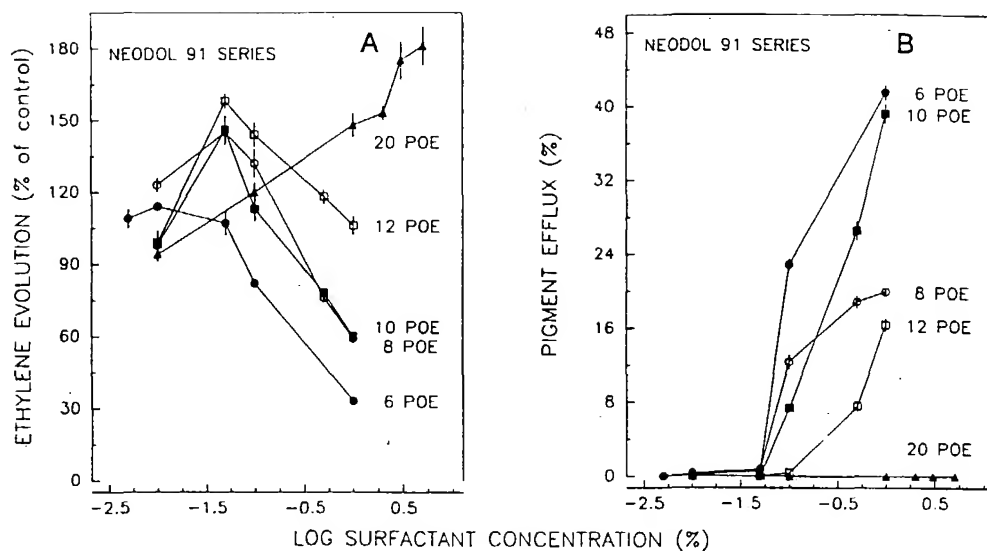
Before detailing our results, a brief overview of ethylene biosynthesis, as well as pigment localization in beet root cells, should be helpful. Ethylene synthesis in plant tissues is believed to be as follows:<sup>19,49</sup> methionine, the general precursor of ethylene, is converted into S-adenosylmethionine (SAM); SAM is then converted, via the enzyme ACC synthase, to ACC; and finally, ACC is converted, via the ethylene-forming enzyme (EFE), to ethylene.

Two comments regarding this sequence are in order. First, the conversion of SAM to ACC is the rate-limiting step.<sup>48</sup> In other words, ACC synthase activity controls ethylene biosynthesis. As mentioned in Section II, we supplied ACC to the beet root discs in our assay to ensure that substrate would not be limiting. Second, the EFE has not been isolated and/or characterized to date.<sup>25</sup> Based on several lines of evidence,<sup>27,28</sup> including studies on surfactant disruption of membranes,<sup>1,2,24,33</sup> the EFE is a highly organized, membrane-bound enzyme. The EFE is probably associated with both the plasma membrane and tonoplast,<sup>49</sup> although the cell wall may also be involved.<sup>26</sup> For a detailed discussion of ethylene biosynthesis, the reader is referred to References 20, 25, 48, and 49.

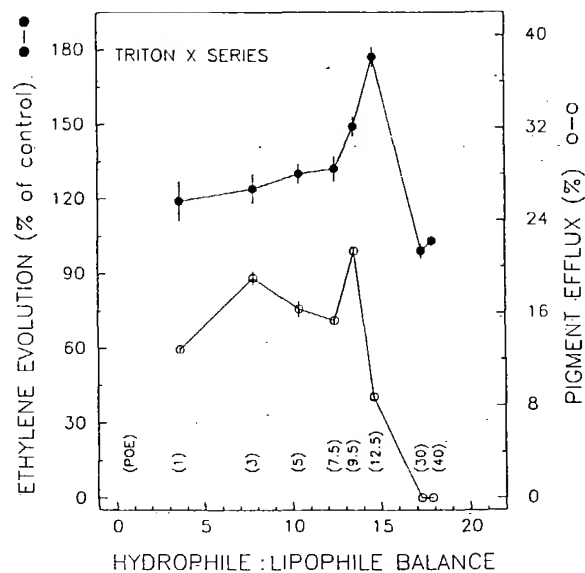
In our bioassay, we monitored the efflux of betacyanins, a group of reddish-violet pigments.<sup>14</sup> They are small molecular weight, nitrogen-containing compounds concentrated in the vacuole. Perhaps the most well-known betacyanin is betanin, which was first crystallized from beet root tissue.<sup>37</sup> In mature beet root cells, the vacuole comprises approximately



**FIGURE 4.** Effect of Tween 20 (A), Ortho X-77 (B), Triton X-100 (C), Duponol (D), Aerosol OT (E), and Arquad C-50 (F) concentration on ethylene evolution and pigment efflux from beet root tissue. Assay conditions: 25°C, pH 7.0, 10 mM ACC, 3-h incubation. Average control (no surfactant) ethylene evolution values (n/h) for Tween 20, Ortho X-77, Triton X-100, Duponol, Aerosol OT, and Arquad C-50 were (SE values in parentheses) 40.0 (1.2), 33.7 (1.3), 33.9 (1.5), 34.3 (1.6), 28.7 (1.0), and 34.3 (1.1), respectively.



**FIGURE 5.** Effect of polyoxyethylene chain length for the Neodol 91 surfactant series, as a function of concentration, on ethylene evolution (A) and pigment efflux (B) from beet root tissue. Assay conditions: 25°C, pH 7.0, 10 mM ACC, 3-h incubation. Average control (no surfactant) ethylene evolution value (nl/h) for Neodols 91-6 and 91-8 was (SE value in parentheses) 40.0 (1.2); for Neodols 91-10, 91-12, and 91-20, the value was 37.3 (1.4).



**FIGURE 6.** Relationship between hydrophile:lipophile balance (HLB) and ethylene evolution and pigment efflux from beet root tissue. Surfactant concentration: 0.1% for ethylene data, 1.0% for pigment data. Assay conditions: 25°C, pH 7.0, 10 mM ACC, 3-h incubation. Average control (no surfactant)-ethylene evolution values (nl/h) for Tritons X-15, X-35, X-45, X-114, X-100, X-102, X-305, and X-405 were (SE value in parentheses) 32.3 (1.3), 32.3 (1.3), 28.7 (1.0), 30.4 (1.4), 33.9 (1.5), 30.4 (1.4), 28.7 (1.0), and 30.2 (0.6), respectively.



70% of the cellular volume (as cited in Reference 29). Although some betacyanin may be found in the cytoplasm because it is the probable site of biosynthesis, the tonoplast is considered to be the main barrier to betacyanin efflux (as cited in Reference 29).

Thus, both responses studied herein are intimately dependent on membrane integrity. If membrane disruption occurs, one would anticipate a loss of EFE activity (and subsequently a decrease in ethylene production) and a leakage of cytoplasmic/vacuolar compounds (pigment efflux) into the incubation medium.

The effect of surfactant concentration on ethylene evolution (percent of control) and pigment efflux (percent) data for six representative surfactants are presented in Figure 4 (A through F). These surfactants represent three different classes of chemistry (based on net molecular charge). Tween 20, Ortho X-77, and Triton X-100 (Figures 4A through C) are nonionic, Duponol and Aerosol OT (Figures 4D and E) are anionic, and Arquad C-50 (Figure 4F) is cationic. These surfactants were selected for presentation because they illustrate the five main response patterns observed in our studies.

Each of the three nonionic surfactants demonstrated unique concentration-dependent behavior. Tween 20 did not induce pigment efflux at any of the concentrations examined (Figure 4A). Ethylene evolution increased slightly over control values, especially at concentrations in excess of 1.0%. With Ortho X-77 at a concentration below the critical micelle concentration (cmc), there was essentially no effect on ethylene evolution or pigment efflux (Figure 4B). As the Ortho X-77 concentration was increased above the cmc, both ethylene evolution and pigment efflux increased. Ethylene evolution reached a plateau as the concentration approached 0.1%, whereas pigment efflux continued to increase with an increase in concentration. With Triton X-100, the ethylene evolution curve was biphasic (Figure 4C). There was a slight increase in ethylene evolution at a pre-cmc concentration of Triton X-100 without an accompanying effect on pigment efflux. While pigment efflux steadily increased with increasing Triton X-100 concentration above the cmc, ethylene evolution reached a peak at 0.05% and then decreased dramatically.

The remaining two response patterns are illustrated by an anionic and cationic surfactant, respectively. Duponol inhibited ethylene evolution but induced marked pigment efflux at concentrations well below the cmc (Figure 4D; although data were limited, Aerosol OT [Figure 4E] also demonstrated this type of response). For Arquad C-50, ethylene evolution was slightly lower than controls at the lowest concentration tested (0.005%) and held constant until the surfactant concentration exceeded 0.1%, then decreased dramatically (Figure 4F). Pigment efflux did not occur until the cmc was exceeded, but then increased linearly with increasing concentration.

All 29 surfactants studied can be categorized into one of the five qualitative response patterns described above (Figure 4 representative in parentheses): (Tween 20), Tritons X-305 and X-405, Neodols 25-30 and 91-20, and Tween 80; (Ortho X-77), Neodol 25-3; (Triton X-100), Tritons X-15, X-35, X-114, and X-102, Tritons N-42, N-57, and N-150, Neodols 91-6, 91-8, 91-10, 91-12, 25-7, 25-9, and 25-12; (Duponol/Aerosol OT), Aerosol OT-B; (Arquad C-50), Arquad 2C-75. Given space limitations, it is not possible to present all of our data. Therefore, for some surfactants, this listing of qualitative responses is all that is given. It should be noted that although we attempted to thoroughly test all of the surfactants used in this study, it is possible that we missed an enhancement and/or inhibition response because either our concentration range was too narrow or our concentration increments were too large.

The Neodol 91 series of linear alcohol (mixture of  $C_{9-11}$  hydrophobe chain lengths) surfactants was selected to illustrate the effect of POE content, as a function of concentration, on ethylene evolution (Figure 5A) and pigment efflux (Figure 5B). For ethylene evolution, a biphasic response was observed for those surfactants with a POE content of 6 to 12 (Figure 5A). At low concentrations (0.01 to 0.05%), ethylene evolution was significantly greater



than in the controls. However, as the concentration increased above 0.05% (to 1.0%), ethylene evolution decreased substantially, with the largest decline being observed for those surfactants with the lowest POE content. In contrast to the other members of the Neodol series, Neodol 91-20 did not demonstrate a biphasic response. Instead, ethylene evolution continued to increase with increasing surfactant concentration.

No significant pigment efflux occurred with the Neodol 91 surfactants at concentrations less than 0.05% (Figure 5B). At concentrations above 0.05%, pigment efflux increased with an increase in concentration except with 91-20, which had no effect over the entire concentration range studied. Efflux was, in general, inversely related to POE content. If one plotted efflux vs. POE content for the 0.1% data, a reasonable linear relationship would be obtained. However, if the 1.0% data were utilized, the relationship between POE content and pigment efflux would not be clear. The reason for a greater response from Neodol 91-10 than from 91-8 at higher concentrations is not clear.

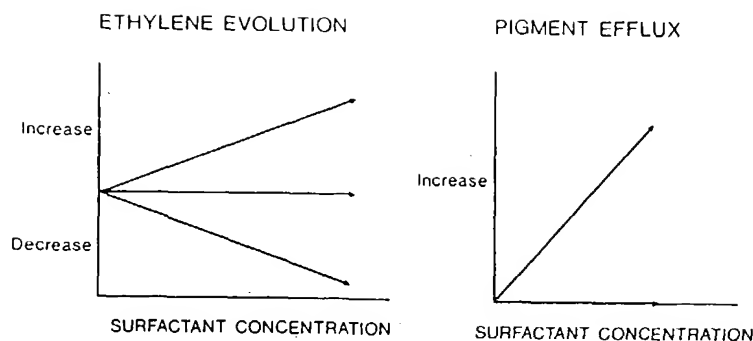
The log cmc values for the Neodol 91 series (Table 1) are between  $-1.6$  and  $-1.4$ . Therefore, as can be seen from Figure 5, maximal stimulation of ethylene evolution for those Neodol surfactants with a POE content of between 6 and 12 occurs around the cmc. This corresponds to the point at which pigment efflux begins. As surfactant concentration increases above the cmc, ethylene evolution decreases while pigment efflux increases, suggesting that both responses are affected via surfactant action on membranes. This is consistent with the observations of others<sup>1,2,24</sup> that membrane (e.g., tonoplast) integrity is required for EFE activity.

Hydrophobe effects on ethylene evolution and pigment efflux are presented in Tables 2 and 3, respectively. For the two alkyl (linear alcohol) surfactants, maximal stimulation of ethylene evolution with the  $C_{9-11}$  hydrophobe mixture was reached at 0.05%, compared to 0.5% for the  $C_{12-15}$  hydrophobe mixture (Table 2). Of the two aryl hydrophobes, nonylphenol caused greater ethylene evolution across the entire concentration gradient examined. In terms of pigment efflux, the smaller hydrophobes ( $C_{9-11}$  vs.  $C_{12-15}$ ; octylphenol vs. nonylphenol) caused greater efflux (Table 3).

These data suggest that simply increasing the lipophilicity of the hydrophobe does not lead to increased biological activity. Indeed, the so-called "Ferguson effect" states that for maximum activity, a balance between lipophilicity and water solubility must be achieved.<sup>38</sup> Factors such as molecular weight, physical size, and the chemical nature and structure of the hydrophobe must also be considered. The importance of the latter point is underscored by the work of Siegel and Halpern,<sup>40</sup> who reported a decrease in alcohol-induced pigment efflux from beet root tissue when the alcohols were branched at the C-1 position.

Hydrophile:lipophile balance (HLB) is commonly used to categorize nonionic surfactants.<sup>4</sup> For polyethoxylated surfactants, HLB values are closely related to POE content. HLB values, in theory, range from 0 (least hydrophilic) to 20 (most hydrophilic). Although HLB value calculations do not factor in concentration (a particular concern for these studies, given the concentration-dependent nature of the ethylene evolution response) or chemical structure, this method of data presentation is useful because it helps visualize relationships between surfactant polarity and biological activity. We selected the Triton X series to demonstrate the relationship between HLB values and ethylene evolution and pigment efflux because of the wide polarity range within this series (Table 1).

At 0.1%, greater ethylene evolution was induced by surfactants having HLB values of 13 to 15 (Figure 6). When the data obtained for these same surfactants at 0.5% were plotted, no qualitative changes were observed. However, when the 1.0% data were utilized, the trend between HLB and maximal ethylene evolution was not readily apparent. For pigment efflux, we selected those data obtained with 1.0% surfactant for graphic presentation (Figure 6). Unlike the ethylene evolution data, pigment efflux for the Triton X series was linearly related to concentration. Therefore, the relationship between HLB and pigment efflux would not



### RELATIONSHIP BETWEEN ETHYLENE EVOLUTION AND PIGMENT EFFLUX

Ethylene Pigment Efflux	Ethylene		
	Increase	No Effect	Decrease
Increase	1,2,9,12,13 14,16,17,18, 19,21,22,23, 24,25,27, 28,29		6,7,8,10,11
No Effect	3,4,15,20,26	5	

FIGURE 7. Schematic illustration summarizing the relationships between ethylene evolution and pigment efflux for the 29 surfactants examined (see Table 1 for listing of numeric code). Categorization based on response observed at 0.1% surfactant.

change qualitatively if data from another surfactant concentration were used. Marked pigment efflux was induced by Triton X-100 (HLB value of 13.5). Buchanan<sup>5</sup> also found that within a series of Triton X surfactants, maximum pigment efflux from beet root tissue was induced with Triton X-100.

It is interesting to compare the HLB values which correspond to the maximum activity in our studies (13 to 15) with those reported by others. Egan et al.<sup>9</sup> observed maximum protein and lipid extraction from mitochondrial membranes at HLB values of 12.5 to 13.5 for a series of Triton X surfactants. As reviewed by Helenius and Simons,<sup>16</sup> studies on the solubilization of microsomes and viral and bacterial membranes have shown that maximum activity is achieved with surfactants whose HLB values are in the range of 12.5 to 14.5. Based on these reports, as well as the data reported herein, maximum membrane interaction appears to occur with surfactants having HLB values in the 12 to 15 range.

Earlier, the surfactants were categorized according to their concentration-dependent ethylene evolution and pigment efflux patterns. Of equal importance, however, are the relationships between ethylene evolution and pigment efflux for each of the surfactants at a given concentration. For this purpose, we compared surfactant data obtained at the 0.1% concentration. We chose this concentration because it represents a common field-use rate for spray applications. As previously mentioned, this type of categorization does not consider concentration-dependent behavior (e.g., biphasic responses).

To summarize, three types of surfactant effects on ethylene evolution were observed: an increase, an inhibition, or no effect (Figure 7). Likewise, with pigment efflux, two types

of surfactant effects were found: an increase or no effect. By creating a matrix of ethylene evolution and pigment efflux response categories, interrelationships between surfactant chemistry and biological activity can be visualized (Figure 7). Clearly, most (18 of 29) of the surfactants increased both ethylene evolution and pigment efflux. All but one were nonionic (Arquad 2C-75 is cationic). In terms of characteristics such as HLB, molecular weight, and cmc (Table 1), members of this group represented a relatively wide spectrum.

Five surfactants (Triton X-305, Triton X-405, Tween 20, Neodol 91-20, and Neodol 25-30) increased ethylene evolution without increasing pigment efflux (i.e., disrupting membrane integrity). All five were nonionic and have relatively high POE contents. One might speculate, as others<sup>11,16,42</sup> have, that surfactants possessing large molecular weights and/or sizes have a reduced level of interaction with cellular membranes, leading to diminished affinity (hydrophobic bonding) and depth of membrane penetration. Curiously, the increase in molecular weight and/or size led to a reduction in membrane disruption (i.e., pigment efflux) but did not diminish the ethylene response.

One surfactant, Tween 80, had no effect on either ethylene evolution or pigment efflux. If one compares Tween 20 with Tween 80 (Table 1), it appears that increasing the hydrophobe chain length from  $C_{12}$  to  $C_{18}$  reduces (eliminates?) surfactant interaction with beet root cell membranes. Sutton and Foy<sup>45</sup> also observed that Tween 20 induced greater pigment efflux from beet root tissue, compared to Tween 80. In terms of the relationship(s) between HLB values and biological activity, these results with Tween 80 are in contrast with those previously discussed. Surfactants with an HLB value of between 12 and 15 were identified as being the most active in terms of membrane interactions. Since Tween 80 has an HLB value of 15.0 (Table 1), this categorization clearly has limitations.

Five surfactants (Duponol, Aerosol OT, Aerosol OT-B, Arquad C-50, and Neodol 91-6) decreased ethylene evolution and increased pigment efflux. Three ionogenic classes of surfactant chemistry are represented by these five compounds, making it difficult to draw conclusions about surfactant chemistry/biological activity profiles. All five surfactants have relatively low molecular weights and would be expected to more readily penetrate into cell membranes. However, this is not the sole factor involved, since other surfactants with similar molecular weights (e.g., Neodol 25-3, Triton X-15) demonstrated different types of behavior (e.g., increased ethylene evolution and pigment efflux).

The empty boxes in Figure 7 also offer useful information. No surfactants increased pigment efflux without affecting ethylene evolution. Similarly, no surfactants decreased ethylene evolution without increasing pigment efflux.

The results of our studies demonstrate that surfactants possess different types and levels of membrane-mediated biological activity. While our studies did not focus on elucidating the basis of surfactant action on plant cell membranes, several observations and points of speculation deserve comment. The mechanism of surfactant action on ethylene evolution (EFE activity) is not clear. As reviewed by Helenius and Simons,<sup>16</sup> low concentrations of surfactant affect (i.e., inhibit, activate, or modify) most membrane-bound enzymes. Interestingly, some membrane enzymes which are activated by low concentrations of surfactant are also inhibited at higher concentrations of the same surfactant. If EFE responded to surfactants in this manner, it could explain some of our ethylene evolution results (e.g., Triton X-100, Figure 4B).

It is generally believed that the surfactant monomer, rather than the micelle, binds/sorbs to proteins.<sup>16</sup> This is particularly true for charged surfactants, where the nature of the charged head group and the length of the alkyl chain are important factors determining the degree of cooperative binding and subsequent conformational (denaturation) change(s). Nonionic surfactants typically do not induce cooperative binding, and therefore are less likely to denature proteins.

Binding/sorption of surfactant by proteins will compete with self-association processes (i.e., micelle formation) as the surfactant concentration reaches/exceeds the cmc.<sup>16</sup> Some insight into surfactant affinity for proteins may therefore be obtained by examining the relationship between surfactant concentration and ethylene evolution. For example, the anionic surfactant Duponol (Figure 4E) significantly inhibited ethylene evolution at pre-cmc concentrations, whereas the cationic surfactant Arquad C-50 (Figure 4F) had little effect on ethylene evolution until the cmc was exceeded. These results suggest that Duponol monomers may have a greater affinity for EFE, compared to Arquad C-50 monomers. This is interesting because cationic surfactants are typically considered more phytotoxic to plant tissues than anionic (or nonionic) surfactants.<sup>13,23</sup> Further detailed binding studies are required to elucidate this point.

It should be noted that in addition to a direct effect on the EFE system, surfactants may affect enzyme activity indirectly.<sup>16</sup> For example, the presence of monomers in the lipoidal membrane could affect membrane fluidity/permeability, leading to changes in the availability of substrate (ACC), cofactor(s), and/or inhibitor(s) for the enzymatic reaction(s). Likewise, the presence of micelles in the incubation medium may also affect assay results, due to micellization (solubilization) of substrate, cofactor(s), and/or inhibitor(s).

In contrast to ethylene evolution, surfactant-induced cellular lysis and subsequent pigment efflux appears to be a relatively straightforward process.<sup>16</sup> Lysis can be divided into five stages: (1) surfactant monomers adsorb to the membrane, (2) the monomers penetrate into the membrane, (3) the monomers disrupt the molecular organization of the membrane, (4) membrane permeability increases, and (5) efflux of cellular contents begins. Since most of the pigment is located in the vacuole, the "membrane" mentioned above (items 1-4) refers to both the plasma membrane and the tonoplast. Each membrane, depending on composition, may well respond to a given surfactant monomer differently.

In conclusion, the beet root assay allows for the simultaneous measurement of surfactant-induced changes in two distinct membrane-associated phenomena. As was clearly evident by the different response patterns of ethylene evolution and pigment efflux, this approach of simultaneously monitoring more than one membrane-associated parameter has merit for a program designed to study the biological activity of surfactants. While several of the general relationships reported herein between surfactant chemistry and biological activity have been observed previously, our data revealed new information on the relationship between ethylene evolution and pigment efflux as related to surfactant/membrane interactions.

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## Chapter 5

**INFLUENCE OF TWO POLYMERIC ADJUVANTS ON  
BIOAVAILABILITY OF GLYPHOSATE IN VISION®  
FORMULATION: RELEVANCE TO RAINWASHING OF  
DEPOSITS FROM FOLIAR SURFACES**

Alam Sundaram

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## ABSTRACT

The influence of two polymeric adjuvants, Sta-Put® and Silwet® Y-6652, on glyphosate washoff from trembling aspen foliage was studied using Vision® formulation at a dosage rate of 0.356 kg of active ingredient (ai) in 25 l/ha. End-use formulations were prepared by adding adjuvant concentration levels ranging from 0.05 to 1.5% v/v to diluted Vision® formulation containing <sup>14</sup>C-glyphosate. Two types of studies were carried out: one for investigating the rate of uptake, foliar washoff, translocation, and bioavailability of glyphosate; and the other for optimizing adjuvant concentration levels to maximize foliar uptake and to minimize washoff, without causing reduction in translocation and bioavailability. Young seedlings were used for the first study using end-use formulations containing 0.05% of the adjuvants. The data indicated that foliar uptake of glyphosate is a slow process since the amount washed off the foliage was >67% at 8 h after treatment and >50% at 48 h. Similar to the foliar uptake, translocation also occurred slowly, only about 2% of the applied amount was translocated in 8 h, and about 10% in 48 h. Nevertheless, there was no evidence of reduced bioavailability because of the presence of the adjuvants at the concentration level used.

Branch tips were used in the second study for treatment of end-use formulations containing 0.05 to 1.5% of the adjuvants, and were harvested at only one time period (48 h). The data indicated that both adjuvants contributed to reduced glyphosate washoff even at the low concentration level of 0.05%. The amount washed off decreased progressively as the adjuvant concentration increased from 0.05 to 1.5%. However, the amount that translocated into the untreated parts of the branch increased initially, passed through a maximum at an adjuvant concentration range of 0.3 to 0.6%, and decreased gradually at higher concentrations of 1.0 to 1.5%. The data thus indicated an optimum adjuvant concentration range beyond which reduced translocation and bioavailability would likely occur. Thus, the study indicated the need to optimize adjuvant concentration levels for every application condition. Otherwise, the rate of uptake and translocation is likely to be impaired, resulting in reduced herbicidal effectiveness.

## I. INTRODUCTION

Rainfall after treatment has been shown to reduce the efficacy of postemergence herbicides.<sup>1,2,4,5,7,9,15</sup> The rain-free period after treatment, required to achieve adequate weed control, varied greatly, depending on the type of formulation.<sup>12</sup> The addition of some polymeric adjuvants has proved to be useful in protecting foliar deposits against washoff<sup>17</sup> and in improving the rainfastness of pesticides.<sup>14</sup> However, certain polymers can cause adverse side effects, such as reduced bioavailability via entrapment of the herbicide molecules in the polymeric structure.<sup>8</sup>

In the present study, aspects of foliar uptake and translocation into a forestry weed species were investigated as a means of assessing the bioavailability of radiolabeled glyphosate (*N*-(phosphonomethyl)glycine, Monsanto Agricultural Products Company, St. Louis, MO). Two polymeric adjuvants, Sta-Put® (Nalco Chemical Company, Naperville, IL) and Silwet® Y-6652 (Union Carbide, Danbury, CT), were investigated at different concentration levels in Vision® (a commercial formulation of glyphosate from Monsanto) formulation. The objective was to optimize the adjuvant concentration that would provide maximum protection against washoff with minimum reduction in bioavailability.

TABLE 1  
Percentage Compositions of Ingredients in the Glyphosate  
Formulations Used in the Preliminary Investigations and  
in Study 1 of the Detailed Investigation

Formulation ingredients	Percentage composition (v/v)	
	Formulation VW	Formulation VWSt-0.05 <sup>a</sup> or VWSi-0.05
Distilled water	42.00	41.95
Vision® (356 g of glyphosate/l)	4.00	4.00 <sup>b</sup>
<sup>14</sup> C-glyphosate <sup>c</sup>	54.00	54.00
Adjuvant	—	0.05

<sup>a</sup> The formulation VWSt-0.05 contained the Sta-Put® adjuvant, whereas the VWSi-0.05 formulation contained the Silwet® Y-6652 adjuvant.

<sup>b</sup> At a concentration level of 4.00 g of glyphosate in 100 ml, the dosage rate is equivalent to 0.356 kg of the active ingredient in 25 l of the formulation per ha.

<sup>c</sup> The radiolabeled product had a specific activity of 10 µCi per milligram of glyphosate in 1.00 ml of solution.

## II. PRELIMINARY INVESTIGATIONS

Preliminary investigations were carried out to examine the adhesive capacity of the Sta-Put and Silwet Y-6652 polymers for glyphosate deposits. <sup>14</sup>C-labeled glyphosate formulations with and without the adjuvants (Table 1) were applied in droplets (each 0.5 µl in volume or 1000 µm in diameter) to glass plate surfaces (7.5 × 5.0 cm), at the rate of 2 µl or four droplets per plate, containing <sup>14</sup>C-glyphosate equivalent to 6000 dpm per drop, using a precision microapplicator (Instrumentation Specialties Company, 4700 Superior, Lincoln, NB).

Four replicate treatments were made for each formulation listed in Table 1. The droplets were washed from the glass plates 48 h later using water (2 × 20 ml for each glass plate); the time duration for washing was maintained at 30 s for each wash (equivalent to 60 s for each plate). The wash liquid was collected in a 50-ml measuring cylinder and an aliquot of 4 ml was added to 16 ml of an aqueous scintillation cocktail (Scinti Verse<sup>®</sup> II, SO-X-12, Scientific Company, NJ). The <sup>14</sup>C-activity was determined by a Beckman LS9000 liquid scintillation counter (LSC) with a built-in automatic external standardization to determine counting efficiency. The range of counting efficiency was 95 to 99%, and the data indicated that both polymers exhibited some degree of adhesive capacity for glyphosate on glass plates. For example, the glyphosate on plates treated with the VW formulation (Table 1) containing no adjuvant was completely washed off in the 40-ml aliquot of water, whereas only about 60% of the applied glyphosate was washed from plates treated with VWSt-0.05, which contained the Sta-Put adjuvant at 0.05% (v/v), and only about 50% was washed from plates treated with VWSi-0.05, which contained Silwet Y-6652. The study thus indicated that both polymers are capable of providing rain protection for glyphosate deposits on target foliage, although Silwet Y-6652 will provide greater rain protection than Sta-Put at equal concentration levels.

In view of these findings, detailed investigations were undertaken to study the effect of different concentrations of the two polymers in Vision formulation on the washoff of glyphosate from treated leaf surfaces of trembling aspen (*Populus tremuloides* Michx.) seedlings

at different time intervals after treatment. Simultaneously, the uptake and translocation of glyphosate into plants were also investigated in two types of studies. Study 1 examined the uptake and translocation into different parts of plants at three different time intervals (up to 48 h) after treatment, using the three formulations listed in Table 1. The objective was to assess the rate of uptake, translocation, and redistribution of glyphosate in different parts of plants with formulations containing the lowest concentration of the adjuvants. Study 2 investigated the uptake and translocation of glyphosate into aspen branch tips at 48 h after treatment, using formulations containing five different concentrations of the adjuvants. The objective was to determine the optimum concentration of adjuvant that would provide the maximum foliar uptake with minimum washoff, and with little reduction in the bioavailability (i.e., translocation into untreated parts of plants) of glyphosate.

### III. MATERIALS AND METHODS

#### A. MATERIALS

##### 1. Study 1 — Uptake, Translocation, and Redistribution

The three glyphosate formulations used in study 1 are listed in Table 1 along with the percentage compositions of the ingredients used with them. The  $^{14}\text{C}$ -glyphosate was purchased from Amersham Corporation, Oakville, Ontario, Canada, and the radiolabeling was on the phosphonomethyl carbon.

##### 2. Study 2 — Optimization of Adjuvant Concentration

Three of the 11 formulations used in study 2 were the same as those listed in Table 1. The remaining formulations contained the same amount of Vision (4.0 parts) and  $^{14}\text{C}$ -glyphosate (54.0 parts) as those listed in Table 1, but the adjuvant concentration was increased to 0.3, 0.6, 1.0, and 1.5 parts, followed by a simultaneous reduction in water levels so that the final volume would still be maintained at 100 parts by volume. Accordingly, formulations containing 0.3% of the adjuvant were described as VWSt-0.3 or VWSi-0.3, those containing 0.6% as VWSt-0.6 or VWSi-0.6, etc.

#### B. METHODS

##### 1. Study 1 — Uptake, Translocation, and Redistribution

The majority of the bioavailable portion of the applied herbicides is known<sup>11,16</sup> to be absorbed into plants within 48 h after treatment. Therefore, the absorption and translocation aspects were studied only up to 48 h.

##### 2. Trembling Aspen Seedlings

Thirty trembling aspen seedlings were removed from the field in which they were grown when the seedling height was about 20 cm, planted in pots, placed in a greenhouse, and maintained under constant conditions of temperature ( $15 \pm 1^\circ\text{C}$ ), photoperiod (16 h of light; 8 h of darkness), and relative humidity ( $75 \pm 7\%$ ) for 4 weeks for acclimatization. At the time of the study, the mean  $\pm$  SD of the height was  $40 \pm 5$  cm ( $62 \pm 5$  cm including the pot), the maximum diameter was  $16 \pm 2$  cm, and all the seedlings had  $16 \pm 3$  leaves. The surface area of the leaves at the middle portion of the crown was  $12.5 \pm 2$  cm<sup>2</sup> per leaf. Twenty-seven seedlings were divided into three groups (A, B and C), each consisting of nine seedlings. Group A received the VW formulation, group B, VWSt-0.05, and group C, VWSi-0.05, respectively. The remaining three seedlings served as controls for measuring the background radioactivity in the plants.

TABLE 2  
Foliar Uptake and Translocation of Glyphosate in Vision® Formulation with and without Two Polymeric Adjuvants — Percentage Distribution of Radioactivity in the Different Samples Analyzed

Sample description	Percentage distribution*								
	VW			VWSt-0.05			VWSi-0.05		
	8 h	24 h	48 h	8 h	24 h	48 h	8 h	24 h	48 h
Treated leaves	21.69	27.55	28.35	30.79	35.55	34.23	29.89	36.55	36.75
Leaves above treated leaves	0.26	0.49	0.93	0.30	0.60	0.90	0.30	0.50	0.80
Leaves below treated leaves	0.24	0.55	1.01	0.24	0.70	1.21	0.40	0.60	1.30
Stem	0.54	1.11	3.77	0.50	1.20	4.20	0.60	1.10	4.30
Root	0.15	1.70	4.21	0.20	2.30	5.41	0.30	2.10	4.41
Plant total	22.88	31.40	38.27	32.03	40.35	45.95	31.49	40.85	47.56
Leaf wash	76.80	68.20	61.13	67.74	59.31	53.54	68.36	58.91	52.08
Soil extract	0.02	0.03	0.05	0.03	0.04	0.06	0.05	0.04	0.06
Grand total	99.70	99.63	99.45	99.80	99.70	99.55	99.90	99.80	99.70
Percent	0.30	0.37	0.55	0.20	0.30	0.45	0.10	0.20	0.30

\* Values represent the mean of three sets of data obtained from three trees. All values were corrected for the  $^{14}\text{C}$  counting efficiency.

### 3. Glyphosate Treatment

A 25- $\mu\text{l}$  aliquot of the formulations listed in Table 1 (containing 0.135  $\mu\text{Ci}$  of  $^{14}\text{C}$ -glyphosate or 300,000 dpm of radioactivity) was applied in  $50 \times 0.5 \mu\text{l}$  drops (1000  $\mu\text{m}$  in diameter) to the middle portion of the crown of eight leaves of each plant at the rate of six drops per leaf for six leaves and seven drops per leaf for two leaves (to provide an average of 0.5 drops per  $\text{cm}^2$ ), using the microapplicator described in Section II.

### 4. Sampling and Analysis

Of the nine seedlings used for each formulation, three were harvested at 8, 24, and 48 h, respectively. Each plant was divided into five segments: treated leaves (TL), leaves above treated leaves (LATL), stem (ST), leaves below treated leaves (LBTL), and root (RT). The TL samples were washed twice with 20 ml of distilled water (for 30 s each time), and the wash liquid (treated leaf wash, TLW) was assayed for  $^{14}\text{C}$  activity as described in Section II. All plant parts, including the treated leaf residue (TLR), were then oven dried for 14 h at  $60^\circ\text{C}$ , weighed, and combusted in a biological sample oxidizer (Packard Oxidizer, Model 306, United Technologies Packard, Packard Instrument Company, Illinois). The evolved  $^{14}\text{CO}_2$  activity was absorbed in vials containing Carbo-sorb® (an aqueous counting scintillant, United Technologies Packard) for the  $^{14}\text{C}$  assay.

The wet soil from the pot was filtered under a vacuum to remove the water, and the residue was washed twice with 20 ml of distilled water. The washings were added to the filtrate, which was then concentrated to a final volume of 3 ml for the  $^{14}\text{C}$  assay, as described above for the aqueous rinse of the TL samples.

The  $^{14}\text{C}$  activity of all samples was determined using the Beckman LSC as described in Section II. The range of counting efficiency was 94 to 98%, and the data in Table 2 were corrected for this. Because few glyphosate metabolites have been reported in plants within 48 h after treatment,<sup>6,10,18</sup> the radioactivity recovered will be referred to as  $^{14}\text{C}$ -glyphosate.

### 5. Study 2 — Optimization of Adjuvant Concentration

To investigate foliar uptake and translocation of glyphosate with several concentrations of the two adjuvants, a large number of seedlings would be required. However, the use of



TABLE 3  
Foliar Uptake and Translocation of Glyphosate into  
Aspen Branch Tips at 48 h after Treatment with the  
Formulations, without and with Adjuvants, at Different  
Concentration Levels — Percentage Distribution of  
Radioactivity

Formulation description	Sample description			
	Treated leaf	Remaining parts	Treated leaf wash	Tap water in vial
VW	31.30*	4.54	64.10	0.06
VWSt-0.05	38.30	5.85	55.75	0.10
VWSt-0.30	42.80	5.85	51.27	0.08
VWSt-0.60	48.30	6.65	44.80	0.25
VWSt-1.00	52.00	3.70	44.20	0.10
VWSt-1.50	58.00	2.50	39.47	0.03
VWSt-0.05	38.55	5.10	56.27	0.08
VWSt-0.30	38.73	7.35	53.67	0.25
VWSt-0.60	42.74	5.10	52.01	0.15
VWSt-1.00	48.15	3.85	47.80	0.20
VWSt-1.50	55.93	2.85	41.02	0.20

\* Values represent the mean  $\pm$  SD calculated from six sets of data obtained from the six branch tips used for each formulation. All values were corrected for the  $^{14}\text{C}$  counting efficiency. Percentage distribution values were calculated as:

$$\% \text{ Distribution} = \frac{\text{Radioactivity recovered in sample}}{\text{Total radioactivity recovered}} \times 100$$

a large number of seedlings would involve extensive labor, time, and cost of materials. To overcome this problem, small branch tips were used in study 2.

Sixty-eight branch tips (each 20 cm long, containing four fully developed young leaves) were clipped from the top portion of the seedlings (one branch from each seedling) which were maintained in the greenhouse, as described in study 1. The underdeveloped young leaves, except the shoots, were removed and discarded, leaving only the four fully developed leaves and shoots in the branch tip. The stem of each branch was immediately placed in a 50-ml plastic vial containing tap water, and the branch was supported upright by tubing and a lid with a hole. Similar branch clippings were tested for their survival rate and growth patterns for up to 7 d in a preliminary investigation prior to the actual study; the branches remained healthy, but showed a small reduction in weight during the first 2 d. However, weight gain was noted from the third day onward, and the plants grew quite well afterward.

Sixty-six branches were divided into 11 groups, G1 to G11, each consisting of six branches. Table 3 lists the different group numbers together with the formulations which were applied to each group. The remaining two branches (group G12) served as controls for measuring the background radioactivity in the branches. A 12- $\mu\text{l}$  volume (containing 144,000 dpm of radioactivity) of each formulation was applied in  $24 \times 0.5 \mu\text{l}$  drops to four leaves (total surface area 50  $\text{cm}^2$ ) at the rate of six drops per leaf. For relevant details, see Section B.3

The six branches used for each formulation were harvested at 48-h posttreatment. This time period was considered adequate for detecting differences in the uptake and translocation patterns between the three formulations used. Each branch was divided into two parts: treated



leaf and the remaining parts. The tap water in the vial was also collected for radioassay to examine glyphosate movement via the stem into the water. The treated leaf was rinsed as described above to provide TLR and TLW. All samples were assayed for  $^{14}\text{C}$ -glyphosate in the same manner as mentioned in Section B.4. These data are given in Table 3.

## IV. RESULTS AND DISCUSSION

### A. STUDY 1 — UPTAKE, TRANSLOCATION, AND REDISTRIBUTION

Data in Table 2 indicate that foliar uptake of glyphosate is a relatively slow process, since more than 67% was washed off into the leaf rinse at 8 h after treatment, irrespective of the type of formulation tested. However, as the exposure duration increased, the uptake gradually increased to 28 to 37%, depending on the adjuvant, and only about 52 to 61% was washed off at 48 h.

Similar to the foliar uptake, the translocation of glyphosate from the treated leaf into other parts of the seedlings was also slow, as only about 2% of the applied amount was translocated at 8 h after treatment, and approximately 98% remained in the treated leaf. However, with the increased exposure, translocation increased gradually and reached 10 to 11% at 48 h (Table 2). Nevertheless, the treated leaf still contained about 88 to 89% of the applied amount, thus indicating incomplete translocation even after 48 h. The amount of radioactivity detected in the stem and root sections increased gradually from the 8-h value, to about four to five times higher at 48 h. The present findings are in agreement with those reported in the literature,<sup>11</sup> although the amount absorbed and translocated was slightly higher in the present study than in those reported.

Regarding the influence of the two polymeric adjuvants on the bioavailability of glyphosate, the present data indicate no evidence of glyphosate entrapment in the polymeric chain, thereby making it less bioavailable. On the contrary, the two adjuvants contributed to a significant increase in foliar uptake, as indicated by an analysis of variance test (ANOVA  $p \leq 0.05$ ), yet the translocated amount seemed to be similar for all three formulations. Consequently, it appears that the increase in foliar uptake does not necessarily indicate an increase in the penetration of glyphosate through the leaf cuticle, since the adjuvants could have simply provided a protective layer over the droplets, thus reducing the amount being washed off during rinsing. Without detailed investigations using extracted plant cuticle,<sup>3</sup> it would not be possible to determine whether the two polymers actually increased the foliar uptake of glyphosate or simply provided a protective film over the droplets. Nevertheless, the present study indicated no evidence of reduced bioavailability of glyphosate at an adjuvant concentration level of 0.05% v/v.

### B. STUDY 2 — OPTIMIZATION OF ADJUVANT CONCENTRATION

The results obtained from the six branch tips used in study 2 for each formulation were subjected to statistical treatment using the Student-Newman-Keuls test (SNK).<sup>13</sup> The data indicated that, on average, about 64% of the applied amount was washed (at 48 h) from the leaf treated with VW, as opposed to about 56% with VWSt-0.05 and VWSi-0.05 (Table 3), thus indicating a significant decrease (SNK error rate  $\alpha \leq 0.05$ ) in the "apparent foliar uptake" because of the presence of the two adjuvants. The amount translocated into the remaining parts of the branch tip was 4.54% for VW, but was slightly higher for VWSt-0.05 and VWSi-0.05. However, as the concentration of the adjuvants increased to 1.5%, the amount of glyphosate that was washed from the treated leaves decreased progressively, whereas the nonwashable residue in the treated leaves increased correspondingly. On the other hand, the amount that was translocated into the remaining parts (i.e., the stem and the new shoots) of the branch tips showed an increase up to an adjuvant level of 0.6%, but

decreased rapidly as the concentration level increased further to 1.5%. Thus, the data clearly indicate the role of adjuvant concentration on the foliar uptake, translocation, and bioavailability of glyphosate. It appears that there is an optimum level of the two adjuvants at which the translocation occurs to a maximum extent, beyond which the translocation process is likely impaired. The reason for this could be that glyphosate is adsorbed and/or trapped into the cross-linked polymeric chain at polymer concentrations greater than 0.6%. The present study demonstrated the need for optimizing the adjuvant concentration for every application condition, because the use of different volume rates would alter the concentration of the surfactant which is already present in the commercial formulation concentrate, and hence the adjuvant concentration would correspondingly require optimization, depending on the volume rate of application used.

## V. CONCLUSIONS

The present findings demonstrated that both Sta-Put® and Silwet® Y-6652 show some potential for providing rainfastness for glyphosate deposits on foliage, since the amount of washable glyphosate was reduced in the presence of the two adjuvants, compared to the amount that was washed off without the adjuvants. Nevertheless, the need to optimize the concentration level of the adjuvants is indicated for every application condition. Otherwise, the active ingredient would likely be less bioavailable as a result of reduced translocation into the active sites of the plants, thus possibly resulting in impaired herbicidal effectiveness.

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## Chapter 6

## A FOLIAR UPTAKE MODEL OF TRICLOPYR

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## ABSTRACT

Foliar uptake of a triethylamine salt of  $^{14}\text{C}$ -triclopyr into field bean (*Vicia faba* L. cv. Maris Bead) leaves was enhanced by the addition of a nonionic organosilicone surfactant, Silwet® L77. The surfactant significantly reduced the surface tension of triclopyr solutions to  $22 \text{ mN m}^{-1}$ , although improved foliar uptake could not be solely attributed to surface tension changes. Fluorescence microscopy of herbicide solutions containing a fluorescent indicator showed that addition of Silwet L77 permitted these solutions to penetrate rapidly into the stomatal pores on the adaxial surface of the bean leaf.

A model of the uptake process for triclopyr and the modifications induced by Silwet L77 has been established. The model assists in determining the mode of action of Silwet L77 and can be used in interpreting the action of other organosilicone surfactants.

## I. INTRODUCTION

The cuticle is the most significant barrier to herbicide absorption into shoot or foliar tissue.<sup>13</sup> Herbicides must penetrate the cuticle in order to gain entry to the plant. The potential pathways of herbicide absorption may be through the cuticle proper and/or through the stomata. If infiltration of active ingredient into substomatal cavities is appreciable, it would be advantageous since:

1. It would reduce the duration of the postspray rain-free of the herbicide.
2. Relatively humid conditions within the substomatal cavity would prolong the time the active ingredient is in solution and, therefore, can be absorbed and subsequently translocated.

Many researchers have shown herbicide entry via stomata to be important.<sup>10,12,17,18</sup> Schonherr and Bukovac<sup>18</sup> found that entry through stomatal pores depends on three main factors: (1) plant surface wettability, (2) stomatal morphology, and (3) solution surface tension. If the surface tension of the herbicide formulation is at or below the critical tension value for the solution and plant surface, instantaneous stomatal entry can occur. Critical surface tension values can be determined for each surface and solution combination.<sup>19</sup> Critical surface tension is defined as the surface tension at which the contact angle is  $0^\circ$  (i.e., cosine of contact angle  $\theta_c = 1$ ). An idea of the major chemical components of the surface can also be deduced from these values.<sup>19</sup>

In aqueous systems such as those containing herbicides, the inherently high surface and interfacial tensions can be reduced by the addition of relatively small amounts of a surfactant.<sup>15</sup> Nonionic organosilicone surfactants are one surfactant group which have been observed to markedly reduce surface tension and enhance the activities of a number of herbicides.<sup>14</sup> The promotion of glyphosate efficacy was explained by the surfactant, Silwet L77, enabling stomatal infiltration of herbicide solutions to occur.<sup>12</sup>

In this study, foliar uptake of an amine salt triclopyr  $\{[(3,5,6\text{-trichloro-2-pyridinyl}) \text{oxy}] \text{acetic acid}\}$ , by field bean was investigated in combination with the nonionic organosilicone surfactant, Silwet L77. Fluorescence microscopy was used to visualize the effect of this surfactant on the foliar uptake process. Surface tension and contact angle relationships were also studied and related to the foliar uptake findings. A computer modeling approach is adopted to describe the triclopyr uptake process by field bean. Such an approach will help to quantify the important features by which Silwet L77 enhances uptake of the herbicide.



## II. MATERIALS AND METHODS

### A. PLANT MATERIALS AND GROWTH CONDITIONS

Field bean seed was pregerminated and potted into 100-mm pots containing a potting mix. Plants were grown in a controlled environment cabinet with the following conditions; day/night temperature 20 to 23/15°C, 15-h photoperiod, 70 to 75% relative humidity, PPFD of 300  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , and a daily watering regime. All experimental procedures with plants were carried out on adaxial leaf surfaces of the third leaves once they had fully expanded.

### B. FOLIAR UPTAKE STUDY

Solutions of  $^{14}\text{C}$ -triclopyr triethylamine were made by adding  $^{14}\text{C}$ -triclopyr acid to a solution of triclopyr amine (360 g  $\text{l}^{-1}$  triclopyr acid as the triethylamine salt) made up to a field equivalent rate of 4 kg of active ingredient (a.i. per hectare in 200 l  $\text{ha}^{-1}$ ). Concentrations of labeled and nonlabeled triclopyr were such that 1  $\mu\text{l}$  of herbicide solution yielded 20,000 to 30,000 dpm (approximately 0.01  $\mu\text{Ci}$ ). Silwet L77 was included at a rate of 0.25% (v/v) in the surfactant treatments. Each plant received 1  $\mu\text{l}$  as four 0.25- $\mu\text{l}$  droplets 2 h after the beginning of the photoperiod. Eight replicate plants per treatment were used.

At various time intervals over a 2-h period, leaf surfaces were washed with 70% methanol into 25-ml volumetric flasks. The percentage of gross uptake was determined by dividing the radioactivity in the methanol wash by the total radioactivity applied. Immediately after the methanol wash, a second leaf wash with 10 ml of chloroform was used to determine the amount of radiolabel in the wax as a percentage of the total applied radioactivity. The percentage net uptake of triclopyr was determined by subtracting the wax uptake value from the gross uptake (i.e., the amount of triclopyr that entered the plant symplast or apoplast). All radiolabeled solutions were counted in 10 ml of Bray's scintillation fluid by a liquid scintillation counter. The results for the foliar uptake of triclopyr into field bean were analyzed as a function of the time from droplet application. A model of triclopyr uptake was proposed from the results.

### C. SURFACE TENSION

Solutions of triclopyr amine were made up in deionized water to a field equivalent rate of 4 kg a.i.  $\text{ha}^{-1}$  in 200 l  $\text{ha}^{-1}$ . Various concentrations of Silwet L77 were added to these amine solutions: 0, 0.005, 0.01, 0.05, 0.1, 0.25, and 0.5% (v/v). All measurement conditions and solutions were held at a constant temperature of 22°C.

Surface tension was measured using an adapted droplet-volume technique described by Taylor.<sup>21</sup> The droplet volumes for each solution were measured by noting the change in the micrometer readings. Clamp stands and weights were used to eliminate vibrations during droplet formation. Using a conversion table of F values,<sup>1</sup> surface tension could be determined on the basis of the droplet volume and the precise diameter of the needle being used. (External needle diameters in these studies were always 2.01 mm, as measured by a traveling microscope.) Twenty replicate droplets were formed from the apparatus for each solution.

### D. CONTACT ANGLES $\theta_A$

The advancing contact angles ( $\theta_A$ ) of herbicide droplets on the adaxial surfaces of bean leaves were recorded using a horizontally oriented traveling microscope. All droplets were 1  $\mu\text{l}$  in size and positioned 5 mm away from the leaf midrib. Solutions of triclopyr amine with or without Silwet L77 were identical to the concentrations used in surface tension measurements. Ten replicate droplets per solution were formed. Temperature and humidity were maintained at 22°C and 70 to 75%, respectively. Advancing contact angles were determined using Mack's<sup>16</sup> formula [ $\theta_A = 2 \tan^{-1} (h/r)$ ], in which the droplet radius (r) and



maximum height ( $h$ ) were measured with an eyepiece graticule in the microscope. Droplet heights and radii were always recorded 10 to 20 s after the drops were applied to the leaf.

Cosines of the contact angles were plotted against surface tension values for each solution to obtain a Zisman plot.<sup>19</sup> The critical surface tension value for the field bean adaxial leaf surface could then be determined by extrapolating a line of best fit for the plotted data, back to where cosine  $\theta_A = 1$ .

### E. FLUORESCENCE MICROSCOPY

Solutions of triclopyr amine with Silwet L77 at 0, 0.10, 0.25, or 0.50% (v/v) plus Uvitex 2B, a fluorescent indicator (Ciba-Geigy), at  $1 \text{ g l}^{-1}$  were prepared. Bean leaves were treated with four 0.5- $\mu\text{l}$  droplets, 5 to 10 mm away from the leaf midrib. At selected times (60 s and 1 h), treated leaves were first rinsed with deionized water, then with 70% methanol. The two rinses were carried out to ensure that no herbicide residue remained on the leaf surface. Rinsed leaves were gently wiped with clean tissue and mounted onto glass slides for observation. Transverse sections through randomly selected, treated leaves were also prepared to visualize the extent of herbicide penetration into the leaf. Herbicide solutions were detected using a Zeiss fluorescence microscope with a UV excitation source (Exciter filter G365, Chromatic beam splitter FT420, Barrier filter LP418). Photomicrographs were obtained using Kodak color negative film (Ektachrome 100 Professional). Five to seven photographs were taken per treatment to capture representative regions of herbicide absorption within the droplet area.

Image analysis was then used to quantify the mean areas of herbicide absorption in each photomicrograph, as shown by the fluorescent indicator. The system was an image analysis package called PC-Semper (Synoptics Ltd., Cambridge, U.K.), with attached camera and video monitors, capable of scanning images of up to  $512 \times 512$  pixels with 256 grey levels. Threshold intensities were selected to obtain a scanned video image as close to the micrograph as possible. The mean values for degree of herbicide absorption were expressed for each treatment as:

1. Area of absorption as a percent of the whole photomicrograph area
2. Absorption area ( $\text{mm}^2$ ) in the whole photomicrograph area

Transformations were performed on the data to validate the ANOVA assumption of equal variances. A square-root transformation of the area ( $\text{mm}^2$ ) and a logit transformation on the percentage area were the most suitable. (The logit transformation was as follows:  $y = \log_{10} [x/(100 - x)^6]$ ). As statistical inferences were made on the transformed data, standard errors of the transformed means are given.

## III. RESULTS

### A. SURFACE TENSION

The surface tension of the triclopyr amine solution with no added surfactant was  $53.4 \pm 1.42 \text{ mN m}^{-1}$ , but this was significantly reduced by the addition of Silwet L77 (Figure 1). At concentrations greater than 0.05% (v/v), there were no significant changes in surface tension from a mean of  $22.8 \text{ mN m}^{-1}$ . Thus, the largest decrease in surface tension occurred with the addition of up to 0.05% (v/v) Silwet L77.

### B. CONTACT ANGLE AND ZISMAN PLOT

A quadratic curve gave the best fit to the relationship between surface tension and the cosine of the contact angle;  $R^2 = 83\%$  (Figure 2). The equation is as follows:

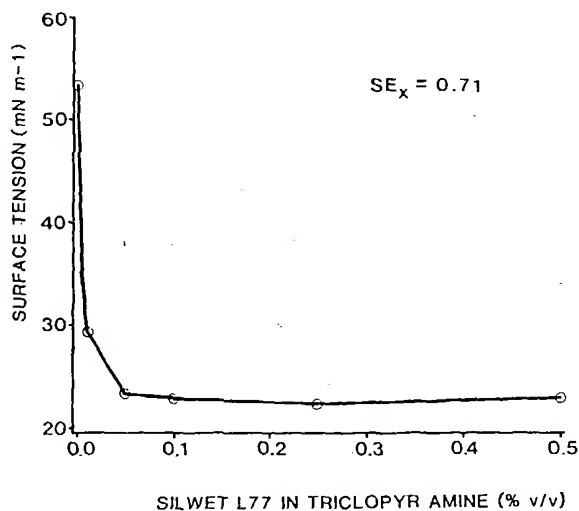


FIGURE 1. Surface tension ( $\text{mN m}^{-1}$ ) of triclopyr triethylamine formulation plus Silwet® L77 surfactant (0 to 0.5%, v/v). A pooled standard error ( $SE_x$ ) of the mean is given.

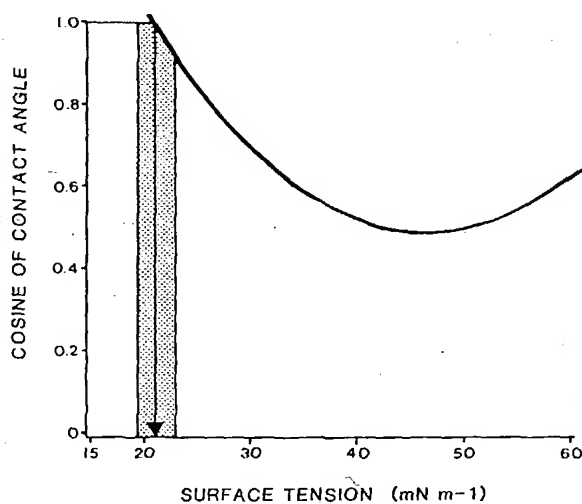


FIGURE 2. The quadratic relationship between surface tension of the triclopyr triethylamine formulation and cosine of the contact angles of droplets placed on the adaxial surface. Mean critical surface tension ( $\gamma_{crit}$ ) value for this surface (when  $\cos \theta_A = 1.0$ ) was  $21.11 \text{ mN m}^{-1}$  with 95% confidence limits shown.

$$y = 2.09 - 0.0655x + 0.000667x^2$$

where  $x$  = the surface tension in  $\text{mN m}^{-1}$  and  $y$  = the cosine of the contact angle ( $\theta_A$ ).

From this, the critical surface tension value ( $\gamma_{crit}$ ) for the adaxial leaf surface of field bean wax calculated as  $21.11 \text{ mN m}^{-1}$ . Parallel curves fitted to provide a 95% confidence limit yielded a  $\gamma_{crit}$  range of  $19.45$  to  $22.87 \text{ mN m}^{-1}$ .

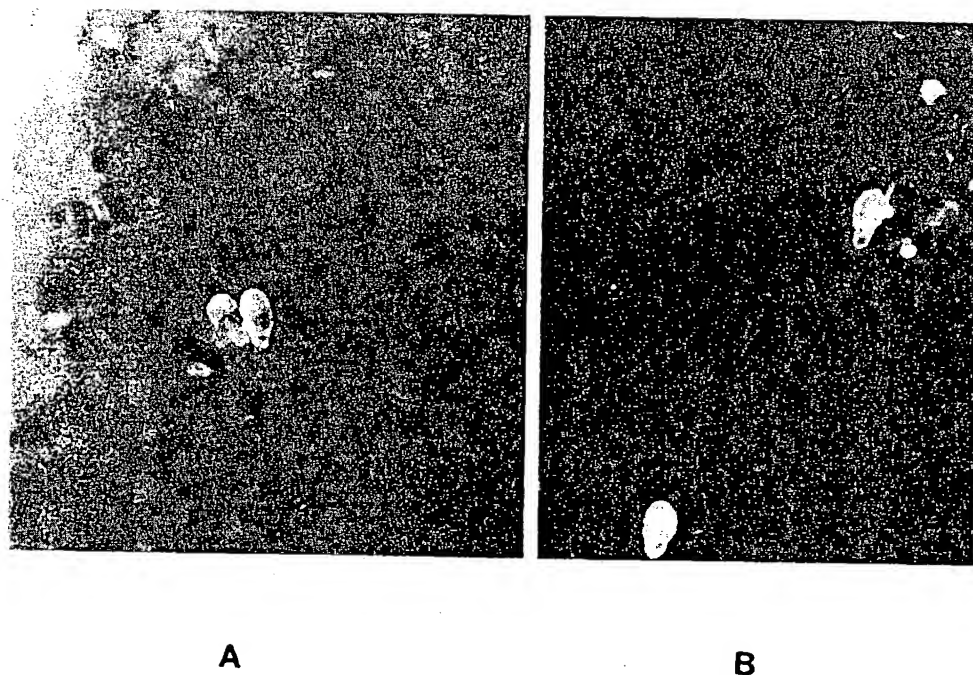


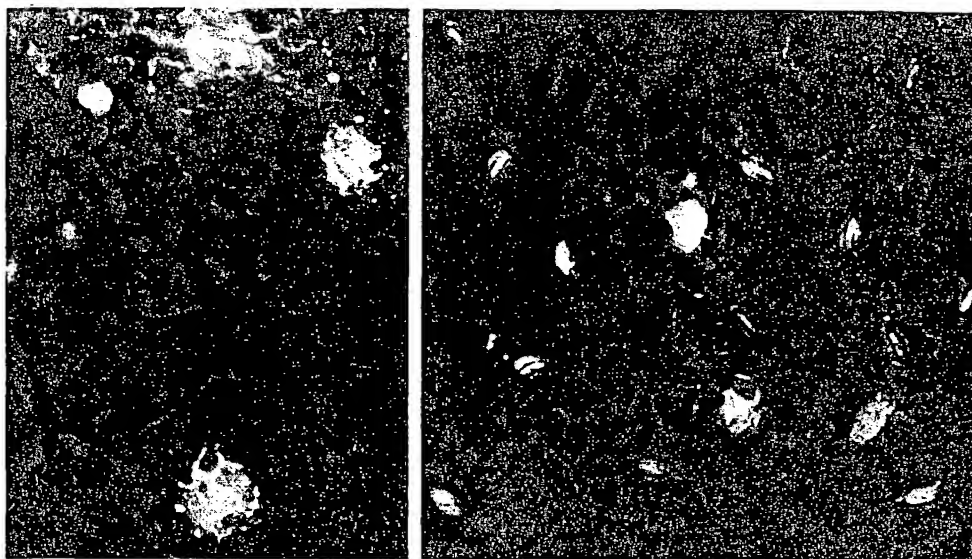
FIGURE 3. Photomicrographs showing typical areas of herbicide absorption after triclopyr amine control solutions + Uvitex 2B indicator were applied to leaves for 60 s (A) or 1 h (B). Glandular trichomes (hairs) and dust particles were the only regions to absorb the formulation. Scale = 100  $\mu$ m.

### C. FLUORESCENCE STUDIES

After both 60-s and 1-h washes, the control herbicide solutions (i.e., no added Silwet L77) had not penetrated the adaxial surface of field bean leaves, as shown by the relative absence of fluorescent dye across their surface (Figure 3). The glandular hairs or trichomes and any dust particles on the leaves were the only parts which appeared to absorb the fluorescent indicator and presumably the herbicide. Transverse sections through leaves also indicated no herbicide penetration into the leaf.

When Silwet L77 was added to the triclopyr amine at 0.1% (v/v), there were some small and infrequent regions of herbicide absorption apparent after 1 h (Figure 4), but nothing after 60 s. Silwet L77 at 0.25 or 0.5% (v/v) were similar, inducing extensive regions of herbicide uptake, after both 60 s and 1 h. Figure 5 shows this for the 0.25% (v/v) Silwet L77 treatment. Herbicide damage to the leaf epidermal cells was often visible after 1 h with these two Silwet L77 rates. This was characterized by large, brightly lit regions of indicator completely covering the site of droplet application (Figure 5C). Transverse sections through the leaf also displayed considerable penetration of fluorescent labeled triclopyr amine with these treatments after both 60 s and 1 h.

Image analysis showed that the mean area of triclopyr absorption was always greater after 1 h than after 60 s within all treatments. The average percentage absorbed for 60-s and 1-h treatments were 6.0 and 18.9%, respectively. This difference between the times was most notable for 0.25 and 0.5% (v/v) Silwet L77 treatments (Table 1). This was also depicted in the photomicrographs.



**FIGURE 4.** Photomicrographs showing typical areas of herbicide absorption after triclopyr amine solutions + 0.1% (v/v) Silwet® L77 + Uvitex 2B indicator were applied to leaves for 1 h. Glandular trichomes (arrow) and some small regions associated with stomatal pores absorbed the formulation. Scale = 100  $\mu$ m.

Herbicide absorption areas were significantly greater when 0.25 and 0.50% (v/v) rates of Silwet L77 were added to the amine formulation. These two treatments were not significantly different from each other (Table 1). Similarly, the control (0%, v/v) and 0.1% Silwet L77 treatments were not significantly different from each other. The interaction between time and solution treatments was not significant.

A range of herbicide absorption patterns was often detected for a single treatment (Figure 5). This was reflected in the large standard errors for some treatments in Table 1. Table 1 provides the transformed means and standard errors of the means on which statistical inferences were based.

#### **D. FOLIAR UPTAKE STUDY**

During the 2-h uptake study, Silwet L77 at 0.25% v/v significantly enhanced the foliar penetration of  $^{14}$ C-triclopyr amine into the adaxial surface of the field bean leaf (Figure 6). The gross and net uptake of solutions without Silwet L77 were significantly less than with Silwet L77 at all stages. A logarithmic transformation was performed on the raw data to obtain uniform errors among the treatments. Linear regressions were then used to describe each treatment (control and Silwet L77) in terms of time. Ninety five percent confidence limits on the two lines showed these to be significantly different.

Wax uptake was always small: less than 1% of applied triclopyr for the control and less than 2% for Silwet L77. Silwet L77-treated leaves tended to have higher wax uptake than the control, although this was only significant after 60 min. Relatively small wax uptake values resulted in net uptake following the same trends as gross uptake.

The mean observed uptake data were used to propose a model of triclopyr uptake (Figure 6). The initial triclopyr uptake rate for the control (i.e., up to 60 min.) was markedly slower than that for the Silwet L77 treatment. During the latter stages (i.e., 60 to 120 min), the rates of uptake for both treatments were similar, as depicted by the approximately parallel



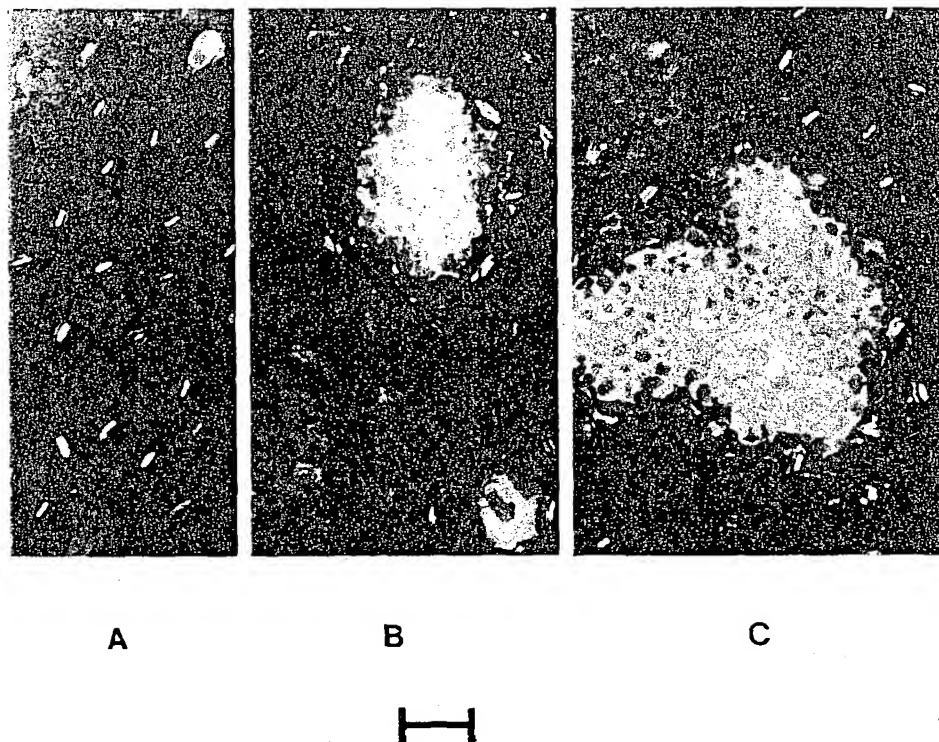


FIGURE 5. Photomicrographs showing the range in typical areas of herbicide absorption after triclopyr amine solutions + 0.25% (v/v) Silwet® L77 + Uvitex 2B indicator were applied to leaves for 60 s. Glandular trichomes had absorbed the formulation and extensive regions of absorption were associated with stomatal pores. Scale = 100  $\mu\text{m}$ .

lines in Figure 6. The biphasic or two-stage uptake suggested by these results are discussed in terms of the possible routes of foliar penetration.

#### IV. DISCUSSION

Surfactants are included in herbicide formulations to enhance the retention and penetration of the active ingredient.<sup>4</sup> Nonionic organosilicone surfactants belong to a group known for their excellent wetting properties,<sup>2</sup> of which Silwet L77 is one. Several researchers have proposed that Silwet L77 promotes entry of herbicide solutions via stomatal pores.<sup>7,12,22</sup> Most surfactants do not appear to act by promoting translocation of herbicides *per se*.<sup>3</sup> Studies with Silwet L77 also suggest that it probably does not enhance efficacy by improving herbicide translocation.<sup>6,9</sup> Whether the promotion of uptake due to Silwet L77 can be totally accounted for by stomatal infiltration is not known.

A significant reduction in surface tension of the triclopyr amine formulation was observed when very small concentrations of Silwet L77 were added (Figure 1). The greatest drop in surface tension occurred up to 0.05% (v/v) Silwet L77. Addition above 0.05% (v/v) did not significantly alter the surface tension, i.e., a plateau surface tension was reached of approximately 23  $\text{mN m}^{-1}$ . This phenomenon is typical of many surfactants in aqueous systems.<sup>4,15</sup>

TABLE 1  
Image Analysis Results from Fluorescence Photomicrographs

Treatment of Silwet L77 (% v/v)	Time	Mean absorption area as % of total area	Mean absorption area (mm <sup>2</sup> )
Control (0% v/v)	60 s	0.94 (-2.02, 0.52)	0.19 (0.43, 0.75)
	1 h	1.00 (-2.07, 0.30)	0.20 (0.43, 0.43)
0.1% Silwet	60 s	0.52 (-2.30, 0.36)	0.10 (0.32, 0.53)
	1 h	1.57 (-1.81, 0.26)	0.31 (0.56, 0.37)
0.25% Silwet	60 s	8.26 (-1.18, 0.19)	1.65 (1.19, 0.28)
	1 h	39.28 (-0.43, 0.19)	7.78 (2.50, 0.28)
0.5% Silwet	60 s	12.65 (-0.86, 0.23)	2.53 (1.57, 0.33)
	1 h	33.62 (-0.32, 0.30)	6.73 (2.55, 0.43)

Note: Values are means for individual treatments. Values in parentheses are transformed mean percentage absorption (logit) or transformed mean absorption area (square root), followed by standard errors of the transformed means.

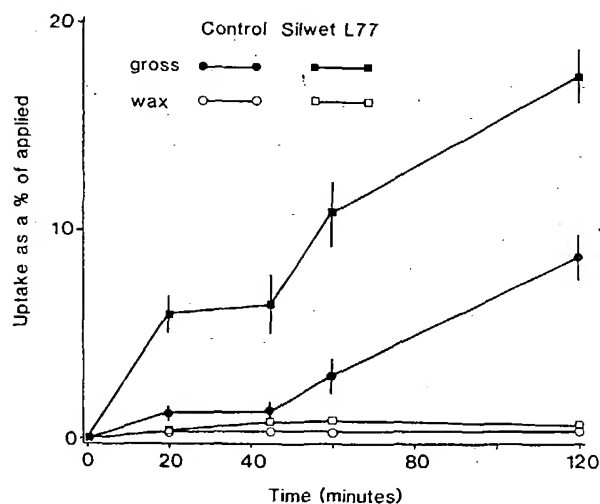


FIGURE 6. The effect of Silwet® L77 (0.25%, v/v) on gross and wax uptake of <sup>14</sup>C-triclopyr triethylamine (expressed as percent of total applied triclopyr). Standard errors of the means are shown as bars on either side of the plotted points.

Droplet contact angles can provide an index of the degree of surface wetting and spreading obtained by that solution on a specific plant surface.<sup>17</sup> As leaf surfaces are generally water repellent (hydrophobic) due to a thin coating of wax over the epidermis, the addition of a surface-active agent (surfactant) can improve the retention of spray droplets by operating at the interface between hydrophilic (droplet) and hydrophobic (plant) phases. In this study,



the cosine of the contact angle on adaxial bean leaf surfaces was plotted against surface tension to produce a Zisman plot. This relationship could then be used to determine the critical surface tension value for that surface and solution, i.e., the surface tension at which the cosine of the contact angle is 1.0 (or  $\theta_A = 0^\circ$ ).<sup>19</sup> For the adaxial leaf surface of field bean, the critical surface tension was 19.5 to 22.9 mN m<sup>-1</sup> (mean of 21.11 mN m<sup>-1</sup>). This was calculated by equating the derived version of the fitted quadratic curve to 1.0. Schonherr and Bukovac<sup>10</sup> obtained a value of 25 to 30 mN m<sup>-1</sup> for the lower (abaxial) leaf surfaces of *Zebrina purpurea* Bruckn. Their critical value may be slightly higher than that for field bean because of differences in the chemical composition and spatial arrangement of the wax constituents.<sup>9,11,19</sup> The surfactant solution studies by Schonherr and Bukovac<sup>18</sup> did not contain triclopyr amine and Silwet L77, which would contribute to a different critical tension value. A tendency of the triclopyr formulations to dissolve the surface molecules of field bean may also explain the lower critical tension value.<sup>11</sup> Scanning electron microscopy supports a surface disruption by triclopyr.<sup>8</sup>

Zisman plots typically form a rectilinear relation between the cosine of the contact angle and the surface tension for a solution series.<sup>19</sup> Determination of the critical surface tension of liquids from such plots has proved useful in describing the spreading behavior of various liquids on a surface. Critical values have also been related to the constitution of various low-energy surfaces. As found with field bean, a critical surface tension of 19.5 to 22.9 mN m<sup>-1</sup> on a hydrocarbon surface is a low value and is typically found with surfaces comprised of closely packed methyl groups.<sup>19</sup>

Although this rectilinear relationship is true for most solutions on most surfaces, the data band may exhibit curvature for values above 50 mN m<sup>-1</sup> on some low-energy surfaces.<sup>19</sup> This phenomenon is believed to be due to weak hydrogen bonds forming between the molecules of liquid and those on the solid surface. This was observed in the studies with adaxial leaf surfaces of field bean and was consistent with the observation that the quadratic curve best described the relationship (Figure 2). Up to 45 to 50 mN m<sup>-1</sup>, the points on the Zisman plot formed a linear band, but above this surface tension, the points tended to curve back up. It has been shown that such curvature is a result of weak hydrogen bonds forming between the molecules of liquid and those in the solid surface.<sup>11</sup> However, attaching importance to the quadratic curve in the region over 45 mN m<sup>-1</sup> should not be done due to only two points influencing the fit here. It was the part of the curve less than 40 mN m<sup>-1</sup> which was important for the calculation of the critical surface tension ( $\gamma_{crit}$ ).

The improved triclopyr uptake observed with Silwet L77 at 0.25% (v/v) in the radiolabeled study cannot be totally explained by the surface tension results. Rate response studies have shown that 0.25 and 0.50% (v/v) rates of Silwet L77 induced significantly greater increase in foliar uptake of radiolabeled triclopyr than 0 and 0.1% treatments.<sup>8</sup> The 0.50% (v/v) rate was not used, as findings suggest that translocation may be reduced at such high rates.<sup>6</sup> In addition, fluorescence studies showed the greatest effect on triclopyr penetration when surfactant rates of 0.25 and 0.50% (v/v) were used. The 0.1% (v/v) rate did not appear to improve the uptake of triclopyr after 60 s, and the improvement after 1 h was considerably less than that obtained with 0.25 and 0.50% (v/v). This was true in spite of the surface tension of all three solutions (0.1, 0.25, and 0.50%, v/v) being essentially the same (Figure 1). This highlights how the interaction of the herbicide-surfactant combination with the plant surface must be of considerable importance.

Retention and penetration of triclopyr amine by the wax was higher than Silwet L77 was present in the formulation. This may be a result of the greater wax area covered by a droplet of herbicide solution when Silwet L77 is present. However, a greater droplet spread due to Silwet L77 was unlikely to be the complete cause of the significant enhancement in overall triclopyr uptake. First, net uptake values (i.e., when <sup>14</sup>C-triclopyr in the wax is

removed from the gross uptake) were still significantly greater when Silwet L77 was present than when it was not. This is a reflection of the wax uptake never exceeding 5.0% of the applied triclopyr. As a result, the removal of wax uptake from gross uptake did not significantly change the net uptake trends from those of gross uptake. Second, if the greater droplet spread was the reason for improved uptake with surfactant, the fluorescent micrographs would have demonstrated similar degrees of herbicide absorption within the droplet regions for both control and Silwet treatments. As this was not observed, Silwet L77 must enhance triclopyr amine uptake by some means other than providing a greater contact area for herbicide droplets.

The uptake promotion due to Silwet L77 was very rapid and occurred within 20 min of application (Figure 6). Field and Bishop<sup>12</sup> found the first 3- to 5-h period to be critical in the enhancement of glyphosate uptake by Silwet L77. After periods of 12 to 24 h, glyphosate uptake with Silwet L77 was not significantly different from the control. Uptake studies of triclopyr amine with or without Silwet L77 over periods up to 24 h also indicated that the first 4-h period was the most important in terms of the rapidity and magnitude of Silwet L77's action.<sup>8</sup> A rapid effect on uptake was further demonstrated by fluorescence microscopy studies. When Silwet L77 was present at optimal rates (either 0.25 or 0.5%, v/v), substantial herbicide solution had penetrated the foliar surface just 60 s after application, whereas control and 0.1% Silwet L77 solutions had not (Figures 3 to 5, Table 1).

Triclopyr amine uptake appeared to follow two quite different phases (Figure 6). During the first 45 min, control solutions showed very low rates of uptake, with gross uptake not exceeding 3.0% of the applied triclopyr. The Silwet L77 (0.25%, v/v) treatment entered relatively quickly during this same initial phase, with 6.0 and 6.4% uptake after 20 and 45 min, respectively. A second phase of uptake occurred after 45 min in which the rates of uptake for control and Silwet L77 treatments were similar. The difference between the two lines was constant and was mainly due to the margin established by the first 20 min. It is proposed that the two phases reflect different pathways or means by which triclopyr entered the leaf. The early phase, taking place in the first hour, may be the period in which instantaneous stomatal infiltration occurred, provided the solution's physical characteristics were suitable. Schonherr and Bukovac<sup>18</sup> stated that to achieve this stomatal infiltration, the surface tension of the herbicide solution must be at or below the critical surface tension for that surface. Since the adaxial leaf surface of field bean has a critical surface tension of 19.5 to 22.9 mN m<sup>-1</sup> (Figure 2), the triclopyr amine solution with 0.25% (v/v) Silwet L77 satisfied this requirement to achieve stomatal entry (Figure 1). Hence, the difference in uptake between the control and Silwet L77 treatment, which was initiated in the first 20 min of uptake, can be attributed to the mass flow and rapid entry of triclopyr via stomata. Fluorescence studies further supported this model, as triclopyr solutions with suboptimal rates of Silwet L77 (0 and 0.1%, v/v) did not significantly penetrate the leaf surface after 60 s or 60 min. In contrast, 0.25 and 0.50% (v/v) Silwet L77 solutions displayed considerably more penetration at both times. Moreover, penetration in these cases was closely associated with stomatal pore regions. Although the 0.1% Silwet L77 treatment should have promoted stomatal infiltration owing to a sufficiently low surface tension (Figure 1), the degree to which this can occur does not equal that of the two higher rates. Thus, surface tension may not be the single determinant in the improvement of triclopyr uptake, due to the addition of the organosilicone surfactant Silwet L77.

Toward the end of the first phase (between 20 and 45 min), the triclopyr uptake rate tended to decrease. This response was particularly noticeable with Silwet L77. It may reflect a saturation of the stomata, more particularly the occlusion of substomatal cavities. The initial rapid penetration rate could not be sustained because the necessary physical gradients could not be maintained as the pore regions approached a satiation level. In the case of the control treatment, any dust, trichomes, or weakened cuticle sites would allow the initial

rapid herbicide entry. Saturation of these sites may be the cause of the apparently small reduction in the control uptake rate between 20 and 45 min.

The second phase uptake pathway (after 60 min) appeared similar for both treatments, since the slope of the curves were the same. At this stage of herbicide uptake (i.e., after 45 min), the process may be one of herbicide diffusion across the cuticle, in which the organosilicone does not seem to play an important role. The rate of herbicide flux through the leaf was similar for both treatments and was equivalent to the flux in phase 1 with the control treatment. This may be a result of the triclopyr solutions requiring time for sufficient attrition of the surface layers and/or of major cellular damage in the epidermal layer. Both changes would allow more rapid movement of the herbicide in phase 2.

Thus, the proposed model of organosilicone-enhanced triclopyr uptake is biphasic. The main effect of the Silwet L77 surfactant was rapid promotion of stomatal penetration into the leaf, occurring within the first 20 min. There was apparent saturation of the substomatal cavities toward the end of the first uptake phase (between 20 and 45 min), reducing the rate of herbicide flux into the leaf. During the early part of phase 1, the significant difference between the control and Silwet L77 treatments was established. Herbicide fluxes in phase 2 were similar for both treatments, which probably reflects a predominance of simple diffusion by both solutions through a partially perturbed leaf surface. Additional research with other organosilicone surfactants and triclopyr suggests that their mode of action may be similar to that of Silwet L77.

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# INFLUENCE OF AN ETHOPROPOXYLATED FATTY AMINE ON THE PENETRATION OF GLYPHOSATE ACROSS ISOLATED TOMATO FRUIT CUTICLES

Simone Santier and André Chamel

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## I. INTRODUCTION

Surfactants are widely used to enhance the performance of foliar applied chemicals, but their effects on foliar uptake are not well understood. Various effects are possible: on spray retention, depending on the wettability of plant surfaces; on penetration, by increasing the area of contact with the leaf; by acting as a humectant, keeping the spray droplets moist for a long time; by improving stomatal penetration; by lowering the surface tension of the spray solution; by facilitating movement along cell walls after entry into the foliage; and by lowering interfacial tensions. Surfactants could also influence cuticular penetration by acting as co-solvents or solubilizing agents, or by affecting permeability. To elucidate the effects of surfactants on penetration across the cuticle, the initial and primary barrier to foliar uptake, we investigated this question *in vitro*, using isolated cuticles. In this chapter, we report results concerning the effects of an ethopropoxylated fatty amine (Armoblen 557®) on the penetration of  $^{14}\text{C}$ -glyphosate, *N*(phosphonomethyl)glycine, across isolated tomato (*Lycopersicon esculentum* Mill. cv. Marmande) fruit cuticles used as a model of the plant cuticle.

## II. MATERIALS AND METHODS

### A. PREPARATION OF ISOLATED CUTICLES

Cuticular discs (diameter: 1 cm) were isolated from mature tomato fruit at 35°C using a mixture of 2% pectinase and 0.2% cellulase (Sigma) at pH 3.8.<sup>2</sup> The cuticles were washed several times with deionized water after their separation, then air dried and stored at room temperature. The efficiency of the separation method was checked by observing the internal surface of the isolated cuticles by scanning electron microscopy (Figure 1).

### B. EXPERIMENTAL CONDITIONS

The experiments were carried out in an air-conditioned room at 20°C, at either low or high relative humidity, according to the diagram given in Figure 2. In the experiments carried out under high-humidity conditions, the cuticles were set out in an impervious box containing a water reserve.

### C. MEASUREMENT OF CUTICULAR PENETRATION

The  $^{14}\text{C}$ -glyphosate as the isopropylamine salt in aqueous solution ( $10^{-4} M$ ) was applied, with and without the surfactant, as a droplet (4  $\mu\text{l}$ ) on the external surface of a cuticular disc placed on an agar block acting as the receiver. Each receiver block was set at the top of a cut syringe (Figure 2), and thus easily recovered using the piston. This device was used to maintain constant hydration of the agar during the penetration. The cuticles were removed and set on new agar blocks several times after the initial deposit. For the experiments under high-humidity conditions, the impervious box was opened and closed rapidly at each change of receiver block. Rapid decrease of the relative humidity inside resulted nevertheless, which was followed by a slower increase until the maximum value was regained. In this case, therefore, the experimental values obtained for the cuticular uptake greatly depended on the frequency of this opening and closing process. At the end of each experiment, the treated surface of the cuticles was washed and the radioactivity of the washings, cuticular discs, and agar blocks determined separately.

### D. CHEMICAL

The ethopropoxylated fatty amine (Armoblen 557) was used because this type of surfactant is recommended for foliar sprays of glyphosate.<sup>7</sup>



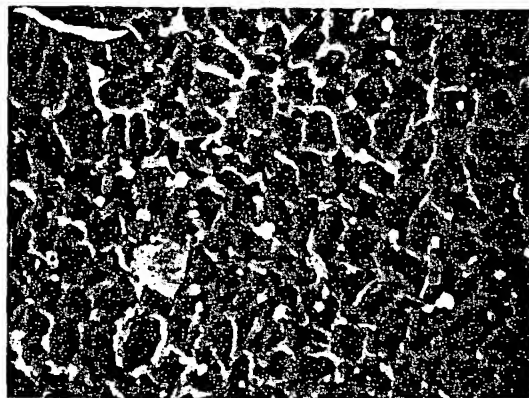


FIGURE 1. Internal surface of the isolated tomato fruit cuticle.

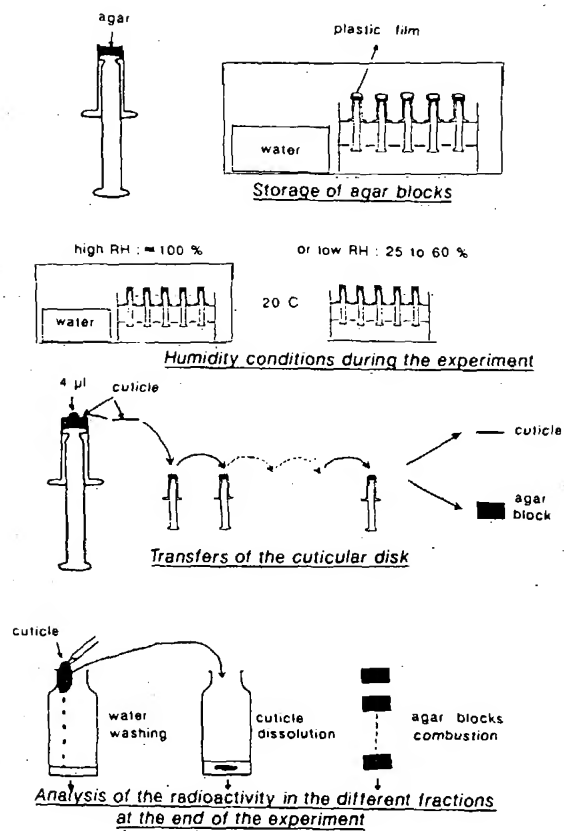


FIGURE 2. Procedure used to study cuticular penetration.

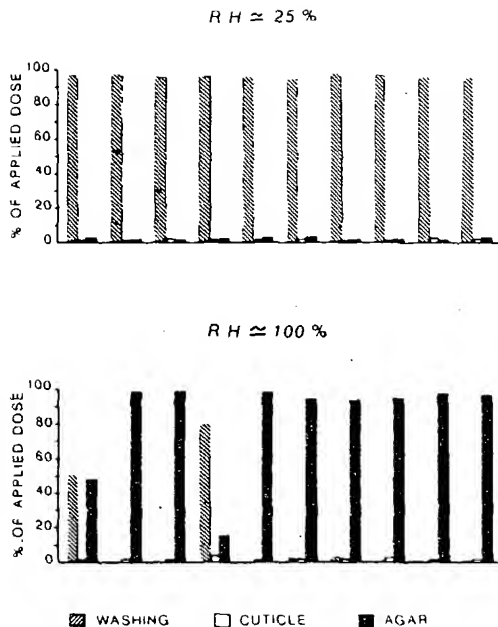


FIGURE 3. Effect of the relative humidity on the cuticular penetration of  $^{14}\text{C}$ -glyphosate through isolated tomato fruit cuticles. The results obtained with ten cuticular discs are reported for each set of humidity conditions. Duration of the experiment, 72 h.

### III. RESULTS

#### A. EFFECT OF RELATIVE HUMIDITY

The penetration of glyphosate across the cuticle greatly depended on the relative humidity and was always considerably greater at high rather than low humidity (Figures 3 and 4). The results in Figure 4 also show that a change from low to high or, conversely, from high to low humidity 24 h after the herbicide deposit, when the droplets were no longer visible, resulted in a drastic change in uptake. Kinetic measurements have allowed discrimination of the penetration before and after the evaporation of the droplet. They have revealed that in most cases of high humidity (Figure 5), diffusion in the receiver block was still very limited at the end of the droplet evaporation, occurring indeed mainly after this time. In the experiment reported in Figure 5, the final value of the penetration obtained at 72 h is lower than that in Figure 3. This difference is due to the reasons mentioned in Section II.

#### B. EFFECT OF SURFACTANT

The effect of the surfactant was investigated under low- and high-humidity conditions.

At high humidity, there was no significant effect of the surfactant on total penetration, but the uptake without surfactant was already very important (Table I). However, an effect of the surfactant during evaporation of the droplet was noted in kinetic experiments. The values of the uptake at the end of evaporation reached 1.9 and 12.7% of the applied dose for the control and 0.5% surfactant, respectively. Evaporation was two to three times faster with the surfactant under these high-humidity conditions.

Under low-humidity conditions, the glyphosate without surfactant diffused weakly across the cuticle. This diffusion was increased by addition of the surfactant at three concentrations: 0.1, 0.5, and 2.5% (Table I). Kinetic measurements revealed that the surfactant increased

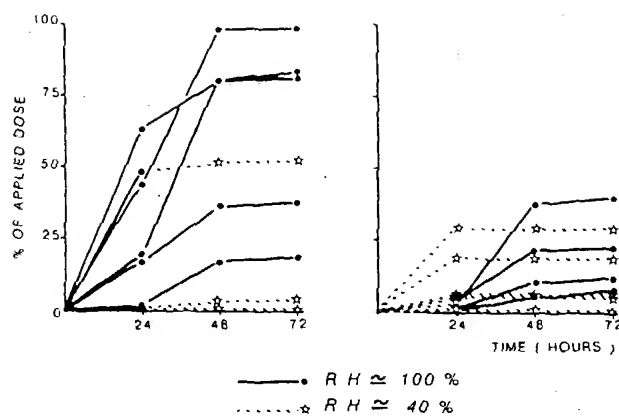


FIGURE 4. Penetration of  $^{14}\text{C}$ -glyphosate through isolated tomato fruit cuticles under different conditions of humidity. Each curve corresponds to a given cuticular disc. The receiver blocks were renewed at 24 and 48 h.

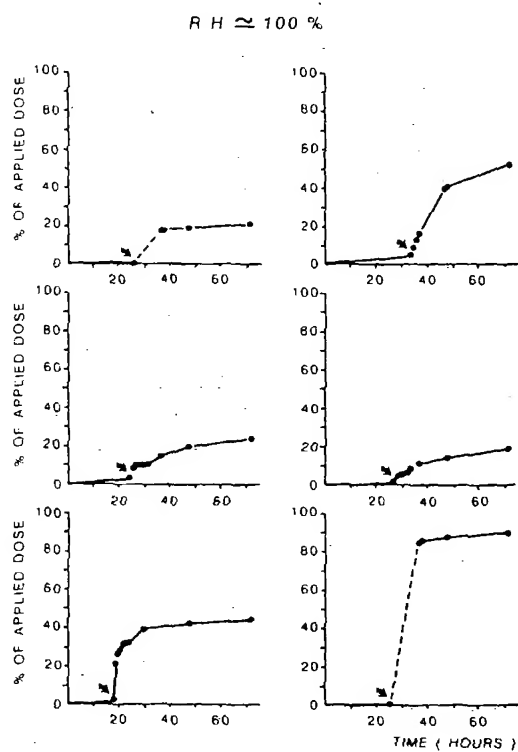


FIGURE 5. Penetration of  $^{14}\text{C}$ -glyphosate through six tomato fruit cuticular discs under high humidity conditions. The arrow indicates the end of droplet evaporation. Each black dot corresponds to a change of receiver block. A dashed line was plotted when there was no renewal of the receiver block during the first hours following droplet evaporation.

the duration of penetration for 2 to 3 d after the disappearance of the droplet (Figures 6 and 7). It was also noted that the penetration rate of glyphosate during droplet drying was higher with the surfactant.

TABLE 1  
Effect of Armoblen 557® on the Penetration of  $^{14}\text{C}$ -Glyphosate Through Isolated Cuticles

Relative humidity (%)	Surfactant conc (%)	Percent of applied dose*					
		Surface 72 h	Cuticle 72 h	Agar			Total
55	0	93.4	1.4	5	0.2	0	5.2 b
	0.1	63.4	1.7	34.4	0.4	0.14	34.9 c
	0.5	50.3	2.6	43.2	3.4	0.48	47 c
	2.5	67.7	2.8	14.3	10.2	5.06	29.5 c
100	0	12.9	9.7	65.9	6	5.5	77.4 d
	0.1	2.9	0.8	81.3	12.1	2.9	96.3 d
	0.5	13.8	1	72.7	8.9	3.9	85.3 d
	2.5	14	0.6	79.8	3.3	2.3	85.4 d

\* Numbers are means of eight replications and are significantly different ( $p < 0.05$ ) when followed by different letters.

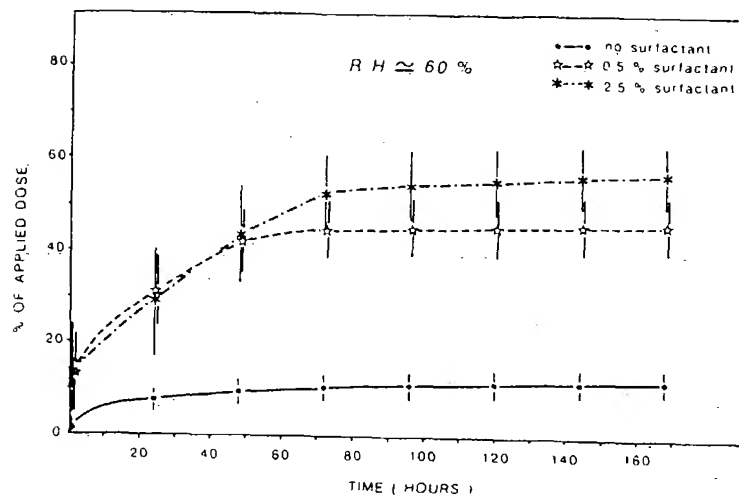


FIGURE 6. Effect of Armoblen 557 on the penetration of  $^{14}\text{C}$ -glyphosate through isolated tomato fruit cuticles under low-humidity conditions. There were 7 to 16 replicates for each value. Confidence interval,  $p = 0.05$ .

#### IV. DISCUSSION

The surfactant Armoblen 557 increases the penetration of glyphosate through isolated tomato fruit cuticles under low-humidity conditions. It appears to extend the duration of penetration considerably after the apparent disappearance of the droplet. The effect of the surfactant may be partly explained by the increase in contact area between the herbicide solution and cuticular surface. The values of this wetted area were approximately 3, 11, 18, and 28 mm<sup>2</sup> with solutions containing 0, 0.1, 0.5, and 2.5% surfactant, respectively. The values of the uptake calculated per unit area, at the end of droplet evaporation, were approximately the same with and without surfactant for both sets of humidity conditions (mean values of the uptake in percent per square millimeter: 0.61 and 0.72, 0.52 and 0.75,

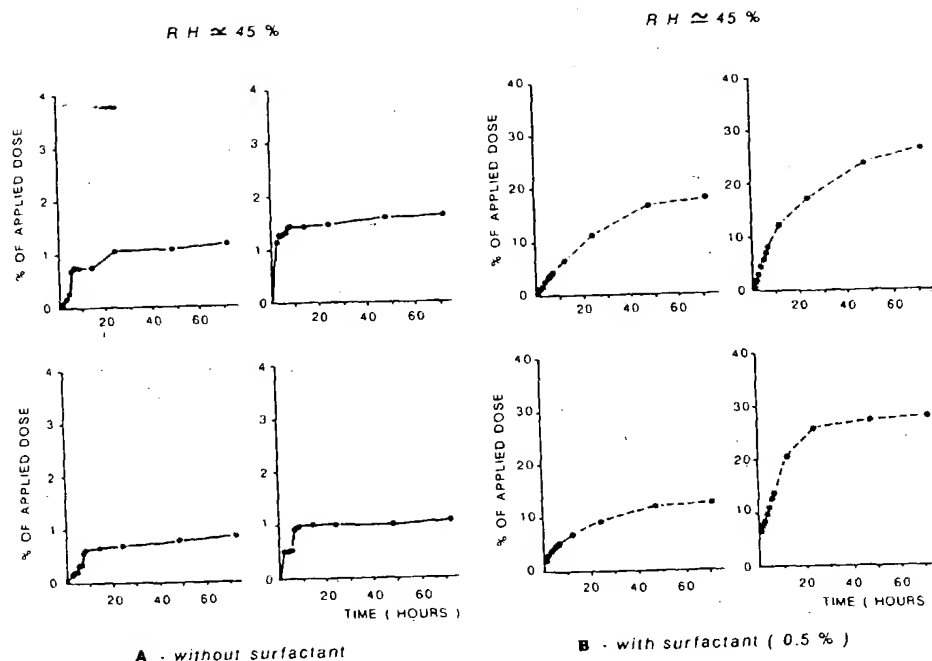


FIGURE 7. Comparison of the penetration kinetics of  $^{14}\text{C}$ -glyphosate, with and without Armoblen 557, through isolated tomato fruit cuticles under low-humidity conditions. Examples obtained with four cuticular discs are reported for each set of conditions: (A) without surfactant; (B) with surfactant. The first black dot on each curve corresponds to the end of droplet evaporation. The Y-scales in A and B differ by a factor of ten.

0.12 and 0.11, all for 0.0 and 0.5% surfactant, respectively, at 100, 60, and 40% relative humidity). The increase in the droplet/cuticle contact area, with the surfactant, leads to a decrease in the volume of liquid per unit area and consequently, of the concentration gradient for the herbicide diffusion. The apparent duration of the droplet evaporation was not clearly affected by the surfactant under low-humidity conditions. After droplet evaporation, there was no clear effect of surfactant on the uptake calculated per unit area. The question of the homogeneity of the distribution of the glyphosate on the deposit area after droplet drying was not resolved, making it impossible to consider the influence of the concentration gradient during this step of the uptake. The surfactant at first allowed diffusion of the herbicide through a greater cuticular area, from a lower volume of liquid and a lower concentration gradient by unit of surface; then, after the apparent droplet evaporation, it would maintain the glyphosate, a hydrosoluble herbicide, in the form of a concentrated aqueous film on the cuticular surface. The surfactant may also have a positive effect on the mobility of the herbicide through the cuticle, e.g., by reducing solute-solute intermolecular interactions. This question could be clarified by measurements of cuticular permeability and the partition coefficient, as previously described.<sup>1</sup> In connection with this, the effect of the surfactant on the cuticular structure should be investigated. The effect of humidity on the foliar uptake of glyphosate, already observed in experimentation on whole plants,<sup>3-6</sup> was confirmed by this study using an *in vitro* model.

## V. CONCLUSIONS

The experimental model presented was successfully used to study cuticular penetration following localized applications of the herbicide solution.

The penetration of glyphosate across isolated tomato fruit cuticles depends greatly on the relative humidity. It is considerably greater under high- than under low-humidity conditions. The surfactant Armoblen 557 (0.1, 0.5, and 2.5%) also facilitates penetration. Its main effect is attributed to the prolongation of favorable conditions on the cuticular surface, allowing the diffusion of glyphosate through a greater area to be continued after the apparent disappearance of the herbicide droplet.

Recent results reveal that the penetration of glyphosate across cuticles isolated from two other plant species is considerably lower than in the case of tomato fruit cuticles. At this stage in the investigation, the reported effects must be confirmed with other cuticular types, and it must be considered whether similar results can be obtained with other surfactants.

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## Chapter 8

INFLUENCE OF THE TYPE AND CONCENTRATION OF  
SURFACTANT ON GLYPHOSATE ABSORPTION; RELEVANCE  
OF DROP SPREADING AND DRYING TIME

Hans de Ruiter, Esther Meinen, and Monique A. M. Verbeek

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## ABSTRACT

The addition of different concentrations (0.005 to 5.0%) of three cationic polyoxyethylene fatty amine surfactants and a nonionic polyoxyethylene nonylphenol surfactant markedly influenced the foliar uptake of glyphosate [*N*-(phosphonomethyl) glycine], applied to winter wheat (*Triticum aestivum* L.) seedlings. At a concentration of 0.5% (w/v), the surfactant Ethomeen®\* T/25 (polyoxyethylene [15] tallow amine) gave the highest absorption rate compared with the other surfactants at 0.5%.

High absorption rates of glyphosate were observed at a concentration of 5.0%. Alone, Ethomeen HT/60 (polyoxyethylene [50] hydrogenated tallow amine) reduced the absorption by a factor of five at high concentrations (2.5 and 5.0%).

The spreading of the drops and their drying time were influenced by surfactant type and concentration. The results indicated that increased drop spreading and a shorter drying time may reduce the absorption of glyphosate. This reduction was observed with Renex®\*\* 688 (polyoxyethylene [8] nonylphenol) and Ethomeen C/12 (polyoxyethylene [2] coco amine) at a concentration of 0.05%, but was not observed at the other concentrations.

## I. INTRODUCTION

The phytotoxicity of glyphosate can be influenced by the type and concentration of the added surfactant.<sup>5,9,14</sup> It has been demonstrated that the type of surfactant influences the foliar absorption of this herbicide.<sup>5,6,8,13</sup> For glyphosate and other herbicides, it is not clear to what extent the surfactant concentration influences absorption. Therefore, in this study, three cationic ethoxylated fatty amine surfactants (Ethomeen C/12, Ethomeen T/25, and Ethomeen HT/60) and a nonionic ethoxylated nonylphenol surfactant (Renex 688) were applied at different concentrations in foliar uptake experiments.

The many factors invoked to explain the influence of surfactants on the foliar absorption include droplet spreading, drying times of droplets, herbicide-surfactant interactions, hygroscopicity of surfactants, permeability of the cuticle, and permeability of the cell membrane.<sup>7</sup> The experimental corroboration for these suggestions is slow in coming because of the complexity of the absorption process.

There is some evidence that the uptake of glyphosate during droplet drying is many times faster than from dry deposits.<sup>12</sup> In this study, the drying times were visually determined to see if there was a correlation between absorption and drying time.

## II. MATERIALS AND METHODS

### A. PLANT MATERIAL

Winter wheat (cv. Arminda) was grown in 9-cm-diameter plastic pots (three plants per pot) filled with a mixture of sand and humic potting soil (1:2). The pots were subirrigated with half-strength Steiner's nutrient solution.<sup>10</sup> The plants were grown in a growth chamber under the following conditions: 15 h light, 18/12°C (day/night), and 70% relative humidity. Light was provided by high-pressure sodium lamps (Philips® 400 W SON/T) and fluorescent lamps (Philips TLD 36 W color 54) to give 80 W/m<sup>2</sup> at leaf level.

### B. SURFACTANTS

The three cationic fatty amine surfactants selected for this study were Ethomeen C/12 (polyoxyethylene [2] coco amine), Ethomeen T/25 (polyoxyethylene [15] tallow amine) and

\* Ethomeen and Arnoblen are the registered trademarks of AKZO chemicals GmbH, Duren, Germany.

\*\* Renex is the registered trademark of ICI Surfactants, Wilton, England.



FIGURE 1. Generalized structure of the ethoxylated fatty amine surfactants (A) and the ethoxylated nonylphenol surfactants (B).

Armoblen®\* NPX containing 50% water and 50% w/v Ethomeen HT/60 (polyoxyethylene [50] hydrogenated tallow amine). The nonionic surfactant was Renex 688 (polyoxyethylene [8] nonylphenol). Each surfactant was a mixture of compounds differing in the length of the alkyl chain and in ethylene oxide (EO) content. Generalized structures of the surfactants are shown in Figure 1.

According to the manufacturers information, in coco amine (Ethomeen C/12), 80% of the alkyl chains range from C12 to C16 in length; in tallow amine (Ethomeen T/25 and Ethomeen HT/60, 95% of the alkyl chains range from C16 to C18 in length, and in hydrogenated tallow amine (Ethomeen HT/60), the unsaturated C-C bond normally present in the alkyl chain is saturated.<sup>1</sup>

### C. ABSORPTION OF $^{14}C$ -GLYPHOSATE

After emergence, the wheat seedlings were thinned to one per pot. Applications were made at the threeleaf stage (14 d after sowing) in the growth chamber. The applications were carried out between 4 and 7 h after commencement of the light period. Methyl-labeled  $^{14}C$ -glyphosate (Amersham, specific activity 2.1 GBq/mmol) was converted to the mono-isopropylamine salt by the addition of isopropylamine in a 1:1 molar ratio.

Nonlabeled technical grade glyphosate (monoisopropylamine salt), surfactants, and demineralized  $H_2O$  were added to the  $^{14}C$ -glyphosate so that the concentration of glyphosate (labeled plus nonlabeled) was 1.3 mM. The surfactants were included on a weight-to-volume basis. The glyphosate solution was applied alone or in combination with surfactant as four 1- $\mu$ l droplets (0.83 kBq) to a discrete area on the adaxial side of the second leaf. The discrete area was marked with waterproof drawing ink. All applications were made using a Burkard Microapplicator PAX 100 fitted with a 50- $\mu$ l syringe and needle coated with polytetrafluoroethylene (PTFE). After 24 h, the treated leaf was removed and washed with 5 ml of water. A 0.5-ml aliquot from the wash was added to 5 ml of scintillation liquid (Hydroluma®, Lumac, LSC B.V., Landgraaf, The Netherlands). Radioactivity was quantified using standard liquid scintillation spectrometry techniques. Absorption was defined as  $^{14}C$  not recovered in the wash, and was calculated as the percentage of  $^{14}C$  applied.

Three experiments were carried out, each according to a  $4 \times 5$  triple rectangular lattice design. Replicate treatments were carried out on different days.

### D. SPREADING AND DRYING OF DROPS

The conditions of application in relation to the plants were the same as described for the absorption studies. Five drops (1  $\mu$ l) containing glyphosate and 0, 0.005, 0.05, 0.5, and 5.0% surfactant were applied to one leaf. Spreading was estimated visually 5 min after application and compared with the spreading of the drop containing glyphosate alone. The time required for drying was also assessed visually. Two experiments were carried out, each with three replications.

### E. SURFACE TENSION

The surface tension of surfactant-containing solutions was measured according to the du-Noüy ring method.

TABLE 1  
Effect of Surfactant Type and Concentration on  
the Foliar Uptake of  $^{14}\text{C}$ -Glyphosate

Surfactant	Absorption of $^{14}\text{C}$ -glyphosate <sup>a</sup> (surfactant conc. %, w/v)				
	0	0.005	0.05	0.5	5.0
No surfactant	38.6 <sup>b</sup>				
Ethomeen C/12		31.0 <sup>c</sup>	23.6	34.9	76.3
Ethomeen T/25		49.3	47.9	58.5	70.7
Ethomeen HT/60 <sup>d</sup>		46.3	31.4	34.5	7.3
Renex 688		45.4	19.9	29.7	63.3

<sup>a</sup> Percent of applied dose.

<sup>b</sup> Absorption values exceeding 54% differ significantly (5% level) from the control treatment.

<sup>c</sup> LSD for all treatments with surfactant is 19.0% (5% level of significance).

<sup>d</sup> The commercial product Armoblen NPX contained 50% Ethomeen HT/60, which means that, in this experiment, Ethomeen HT/60 was applied at 0.0025, 0.025, 0.25, and 2.5% (w/v).

### III. RESULTS

#### A. ABSORPTION OF $^{14}\text{C}$ -GLYPHOSATE

The results of a representative experiment are shown in Table 1. The significance at the 5% level is poor. However, most of the nonsignificant differences between the treatments shown in Table 1 were also observed in two other separate experiments and, therefore, these differences were also considered in the discussion. Ethomeen HT/60 was applied at a half-rate in the experiment shown (Table 1), as the commercial product Armoblen NPX contained 50% water. In two other experiments with double rates of this product, the same trends were observed. None of the surfactants influenced the absorption at a concentration of 0.005%. At 0.05%, Ethomeen C/12 and Renex 688 reduced the absorption. At 0.5%, Ethomeen T/25 gave the highest absorption rate. At this concentration, the absorption rates of Renex 688 and Ethomeen C/12 were enhanced, compared with the rates at 0.05%. At a surfactant concentration of 5%, all surfactants except Ethomeen HT/60 gave a high absorption. Addition of Ethomeen HT/60 at the highest concentration inhibited absorption almost completely.

#### B. SPREADING AND DRYING TIMES OF DROPS

At a surfactant concentration of 0.005%, spreading and the drying times of the drop were the same as for drops containing glyphosate alone (Table 2). At 0.05%, Ethomeen C/12 and Renex 688 enhanced the spreading of the drops, and this probably caused the greatly reduced drying time. Ethomeen T/25 and Ethomeen HT/60 had little, if any, influence on the spreading of the drops. The drying time was longer for Ethomeen T/25 at 5.0% and Ethomeen HT/60 at 0.5 and 5.0%. The latter surfactant even prevented complete drying during the 24 h after the application. These two surfactants appear to retain a relative large amount of water compared with Ethomeen C/12 and Renex 688.

#### C. SURFACE TENSION

Measurement of the static surface tension showed that Ethomeen C/12 and Renex 688 reduced the surface tension much more than the other two products. The critical micelle

TABLE 2  
Effect of Surfactant Type and Concentration on the Drying Times  
and Spreading of Drops

Surfactant	Drying time (min) and spreading (surfactant conc. %, w/v)				
	0	0.005	0.05	0.5	5.0
No surfactant	45.6 (3.8)				
No surfactant	—				
Ethomeen C/12		45.1 (4.9)	16.4 (1.6)	7.7 (1.8)	5.2 (1.3)
Ethomeen C/12		—	+	++	++
Ethomeen T/25		45.9 (4.8)	45.2 (5.4)	44.0 (5.1)	± 180 <sup>a</sup>
Ethomeen T/25		—	±	±	±
Ethomeen HT/60		48.7 (4.1)	50.2 (2.9)	<sup>b</sup>	<sup>b</sup>
Ethomeen HT/60		—	—	—	—
Renex 688		42.7 (3.9)	20.9 (2.5)	19.4 (3.7)	18.6 (3.2)
Renex 688		—	+	+	+

Note: SD (n = 6) in parentheses; — spreads like water; ±, some spreading; +, spreads more than water; ++, spreads much more than water.

<sup>a</sup> Exact drying time difficult to assess visually.

<sup>b</sup> The drops were still present 24 h after application.

TABLE 3  
Surface Tension-Reducing Ability and HLB Values of the Surfactants

Trade name	Chemical description	Critical micelle concentration <sup>a</sup> (cmc) (%, w/v)	γ at cmc (mN m <sup>-1</sup> )	HLB <sup>b</sup>
Ethomeen C/12	Ethoxylated (2) coco amine	0.004	28.4	10.2
Ethomeen T/25	Ethoxylated (15) tallow amine	0.01	41.9	19.3
Ethomeen HT/60	Ethoxylated (50) h.c. tallow amine	0.1	48.1	19.7
Renex 688	Ethoxylated (8) nonylphenol	0.01	31.3	12.3

<sup>a</sup> Measured at 25°C.

<sup>b</sup> Hydrophile-lipophile balance (HLB) according to the manufacturer's information.<sup>1,2</sup>

<sup>c</sup> Hydrogenated.

concentration was 0.004% for Ethomeen C/12, 0.01% for Ethomeen T/25 and Renex 688, and 0.1% for Ethomeen HT/60 (Table 3).

## IV. DISCUSSION

### A. GLYPHOSATE ABSORPTION

#### 1. Surfactant Type and Concentration

It has been demonstrated that glyphosate absorption depends on the type of surfactant and the surfactant concentration. At a concentration of 0.5%, the surfactant Ethomeen T/25 containing 15 mol of EO enhanced the absorption more than Ethomeen C/12 containing 2 mol of EO and Ethomeen HT/60 containing 50 mol of EO. If it is assumed that the difference between the hydrophobic moiety of Ethomeen C/12 and the hydrophobic moiety of the other two alkyl amine surfactants (mentioned in Section II) has a minor influence, this result agrees with published data for the foliar uptake of 2D-glucose<sup>11</sup> and paraquat<sup>4</sup>



using other types of surfactants. In those experiments, maximum absorption was also observed with surfactants containing an intermediate number of EO groups.

Under our experimental conditions, the nonionic surfactant Renex 688 had much less ability to enhance the glyphosate absorption than the cationic surfactant Ethomeen T/25 (Table 1).

A similar result was found with a study on glyphosate absorption in field bindweed (*Convolvulus arvensis* L.).<sup>8</sup> The cationic surfactant MON 0818 (polyoxyethylene tallow amine) enhanced the absorption, whereas the nonionic surfactant Tween 20 (polyoxyethylene [20] sorbitan monolaurate) had no significant influence.

An evaluation of the ability of surfactants to enhance glyphosate toxicity to common milkweed (*Asclepias syriaca* L.) and hemp dogbane (*Apocynum cannabinum* L.) revealed that cationic surfactants (ethoxylated amine type) were generally more effective than the nonionic surfactants.<sup>14</sup>

To what extent the differences mentioned are due to the charge of the surfactant molecules or to other chemical characteristics remains to be elucidated by developing insight at the molecular level.

## 2. Drop Spreading and Drying Time

The spreading of the drops on the surface of wheat leaves (which are difficult to wet) was influenced most by Ethomeen C/12 and Renex 688 (Table 2). The property of these products to reduce the surface tension of the solution much more than the other two surfactants (Table 3) probably accounts for this result. Enhancement of the concentration of Ethomeen C/12 increased spreading and shortened the drop drying time, whereas the surface tension of the solutions containing 0.05, 0.5, and 5.0% Ethomeen C/12 and glyphosate (1.3 mM) was the same. The spreading of a drop is also influenced by the surface tension of the solid-liquid interface and the surface tension of the solid.<sup>3</sup> Reduction of the surface tension of the solid-liquid interface at concentrations of Ethomeen C/12 higher than the critical micelle concentrations (Table 3) may possibly account for the increased spreading. However, other factors may also be relevant, as the dynamics of drop spreading on a solid surface are not completely understood. At a surfactant concentration of 0.005%, the spreading and drying time of the drop remain unchanged. The influence of the surfactants on the absorption of <sup>14</sup>C-glyphosate at this concentration was similar. At a concentration of 0.05%, the increased droplet spreading and shorter drying time observed with Ethomeen C/12 and Renex 688 may explain the reduced absorption of glyphosate if it is assumed that a shorter drying time leads to more rapid immobilization of glyphosate on the leaf surface. At the higher surfactant concentrations (0.5 and 5.0%), absorption with Renex 688 and Ethomeen C/12 was enhanced, notwithstanding the further increased spreading and shorter drying time observed with Ethomeen C/12. This effect may result from the influence of the surfactant on cuticle permeability, the influence on the underlying tissue, or the ability of the surfactants to retain water in the film of surfactant that covers the leaf surface after droplet drying. These factors may also lead to enhanced absorption in the presence of Ethomeen T/25, because this surfactant has little, if any, effect on droplet spreading or drying time (except for Ethomeen T/25 at 5.0%).

Ethomeen HT/60 did not influence the drop spreading and drying time at concentrations of 0.0025 and 0.025% (Table 2). At concentrations higher than 0.025%, the drop did not dry under our experimental conditions. Glyphosate absorption at 0.25% has the same level as measured without surfactant, but at 2.5%, the absorption was strongly inhibited. The results of this study do not indicate what mechanism causes the hindered glyphosate diffusion into the plant tissue when this long EO-chain surfactant is applied at a high concentration.



At present, there is little information on the relationship between foliar absorption and drying times.<sup>12,15</sup> This study indicates that spreading and drying time can be relevant uptake-determining factors. However, to verify the tentative conclusions of this study, more data are required on absorption soon after droplet application and on drying times at different humidities. The influence of the EO content on the retention of water in the film of surfactant covering the leaf surface after visible drying needs more attention, as this retention may influence the absorption of water-soluble compounds. The events in the drying deposits are not the only factors determining the absorption of a compound. Nevertheless, we believe that more insight will lead to generalizations useful for the development of improved formulations.

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## Chapter 9

**THE EFFECT OF A RANGE OF NONYLPHENOL SURFACTANTS  
ON CUTICLE PENETRATION, ABSORPTION, AND  
TRANSLOCATION OF WATER-SOLUBLE AND NON-WATER-  
SOLUBLE HERBICIDES**

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Chandrasena

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## ABSTRACT

The effect of a range of nonylphenol surfactants containing 4 to 14 mol of ethoxylate (EO 4 to 14) was tested on the uptake and distribution of  $^{14}\text{C}$ -asulam {methyl[(4-amino-phenyl)sulfonyl]carbamate} or  $^{14}\text{C}$ -diflufenican {(N-[2,4-difluorophenyl]-2-[3-trifluoromethylphenoxy]-3-pyridine carboxamide)}. Four 0.5- $\mu\text{l}$  droplets were applied to leaves of brackenfern (*Pteridium aquilinum* L. Kuhn) and common chickweed (*Stellaria media* L.), the herbicidal dose being equivalent to normal field rates. Results show that irrespective of surfactant, uptake and translocation of asulam (hydrophilic) was greater than diflufenican (lipophilic), cuticle retention of the latter being considerably greater than asulam. The uptake of asulam was generally enhanced by surfactants of EO 4 to 10, optimum EO 8, while that of diflufenican was significantly enhanced only by EO 4. The results are discussed in relation to the criteria determining penetration of the cuticle and subsequent transport within the plant.

## I. INTRODUCTION

The surface of plant shoots is covered by a lipoidal cuticle which restricts water loss from the plant and acts as a barrier to the penetration of foliage-applied compounds, particularly those having polar characteristics. The outer wall of the epidermal cells is covered by a "cuticular membrane" composed of polymeric cutins with embedded waxes ("cuticular waxes") and an outer deposit of generally structured waxes ("epicuticular waxes").<sup>4,5</sup> The physicochemical properties of these waxes may be very important in determining the wettability of the leaf surface.

Surfactants may enhance cuticle retention and penetration due to a number of functions, including reduction in surface tension, which reduces the droplet contact angle and enhances spray retention, wetting, and spreading. They also may act as humectants, maintaining the active ingredient (a.i.) in the aqueous phase for a longer period, or may possess solubilizing properties which facilitate partition of the a.i. from the solid to liquid phases. In addition, the surfactant may facilitate permeability of the plasmalemma,<sup>10</sup> and this may increase herbicidal efficacy. There is evidence that certain surfactants may enter the leaf tissues, and the elucidation of the relationship between structure and phytotoxicity has been investigated by Silcox and Holloway<sup>8</sup> and Lownds and Bukovac.<sup>7</sup>

The aim of the present study was to examine the effect of a range of ethylan surfactants having differing numbers of ethylene oxide (EO) groups on the uptake and translocation of hydrophilic (asulam) and lipophilic (diflufenican) herbicides.

The test species used in this study are known to be difficult weeds and to present particular control problems. Common chickweed is regarded as a difficult annual species of arable crop while brackenfern is a notorious weed of upland pastures, spreading by growth of the underground rhizome system. The effect of a range of nonylphenol surfactants on the uptake and translocation of asulam and diflufenican has been investigated; these herbicides were selected on the basis of their very different water/lipid solubilities.

## II. MATERIALS AND METHODS

### A. PLANT TISSUES

Bracken rhizomes, cut into 15-cm fragments and planted in John Innes II compost mixed with bracken litter, were placed in a greenhouse. Subsequently, uniform fronds were selected and pinnae removed from the base of mature fronds. The stem of each pinna was inserted

TABLE I  
Nonylphenol Surfactants EO 4 to 14

EO	Compound name	Manufacturer
4	Ethylan 44	Lankro Chemicals
5.5	Ethylan 55	Lankro Chemicals
6.5	Ethylan 77	Lankro Chemicals
8	Ethylan TU	Lankro Chemicals
10	Synperonic NP 10	ICI
12	Ethylan DP	Lankro Chemicals
14	Lutensol AP 14	BASF

into a vial containing 8 ml of distilled water. A photosynthate "sink" was achieved by covering the apical pinnules with aluminum foil. The explants were placed in a growth cabinet for 24 h prior to herbicide treatments (normally  $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ; [RH],  $75\% \pm 5\%$ , 14-h photoperiod).

Chickweed seeds were planted in 7-cm pots in John Innes II compost and grown to the cotyledon state in the greenhouse; no sink was created in this species. The potted plants were placed in the growth cabinet for 24 h prior to treatment.

#### B. HERBICIDES AND ADJUVANTS

The  $^{14}\text{C}$ -asulam (sodium salt) used was ring labeled with a specific activity of  $10.1 \text{ mCi mmol}^{-1}$  ( $44 \mu\text{Ci mg}^{-1}$ );  $^{14}\text{C}$ -diflufenican was pyridine-ring labeled with a specific activity of  $2.0 \text{ mCi mmol}^{-1}$  ( $5.1 \mu\text{Ci mg}^{-1}$ ). The relative solubilities of asulam in water and acetone were 4 and  $300 \text{ g l}^{-1}$ , respectively; the relevant figures for diflufenican were 0.05 ppm and 10%, respectively. A range of nonylphenol surfactants containing 4 to 14 mol of ethoxylate (EO 4–14) were used as adjuvants at a concentration of 0.1% (Table 1).

$^{14}\text{C}$ -asulam and  $^{14}\text{C}$ -diflufenican were applied in solution at the equivalent of field rates ( $7.5 \text{ l/300 l}$  and  $200 \text{ g/200 l ha}^{-1}$ , respectively). In the case of bracken, eight  $0.5\text{-}\mu\text{l}$  droplets of the appropriate herbicide were applied to the basal pair of pinnules (total of  $4 \mu\text{l}$ ); an equivalent amount was applied to the cotyledons of common chickweed.

After 48 h, the plants were harvested, and the treated tissue was separated from the untreated and washed in 3 ml of water + acetone (2 min) and 2 ml of chloroform (30 s) to remove  $^{14}\text{C}$ -residues associated with the surface or cuticle waxes. The treated and untreated regions were dried at  $50^{\circ}\text{C}$ , weighed, wrapped in filter paper, pelletized, combusted (Packard Tricarb Sample Oxidizer, B306), and the  $^{14}\text{CO}_2$  formed was trapped in 8 ml of Carbosorb® II and dissolved in 10 ml of Permafluor scintillant for radioassay.

The data obtained were subjected to analysis of variance, and where relevant, Duncan's multiple range test (D test).

### III. RESULTS

The effect of the ethylan series on absorption and translocation of  $^{14}\text{C}$ -asulam by bracken fern is shown in Figure 1A. Absorption was significantly enhanced by surfactants of EO 4 to 10, EO 8 being optimum; sink accumulation followed a similar pattern. Calculation of the ratios of absorption/surface + wax residues (A/R), sink accumulation/absorption (S/A), and translocation (sink + nonsink)/absorption (T/A) are shown in Figure 1B. The results emphasize the importance of surfactant EO in relation to absorption, effects on translocation being secondary.

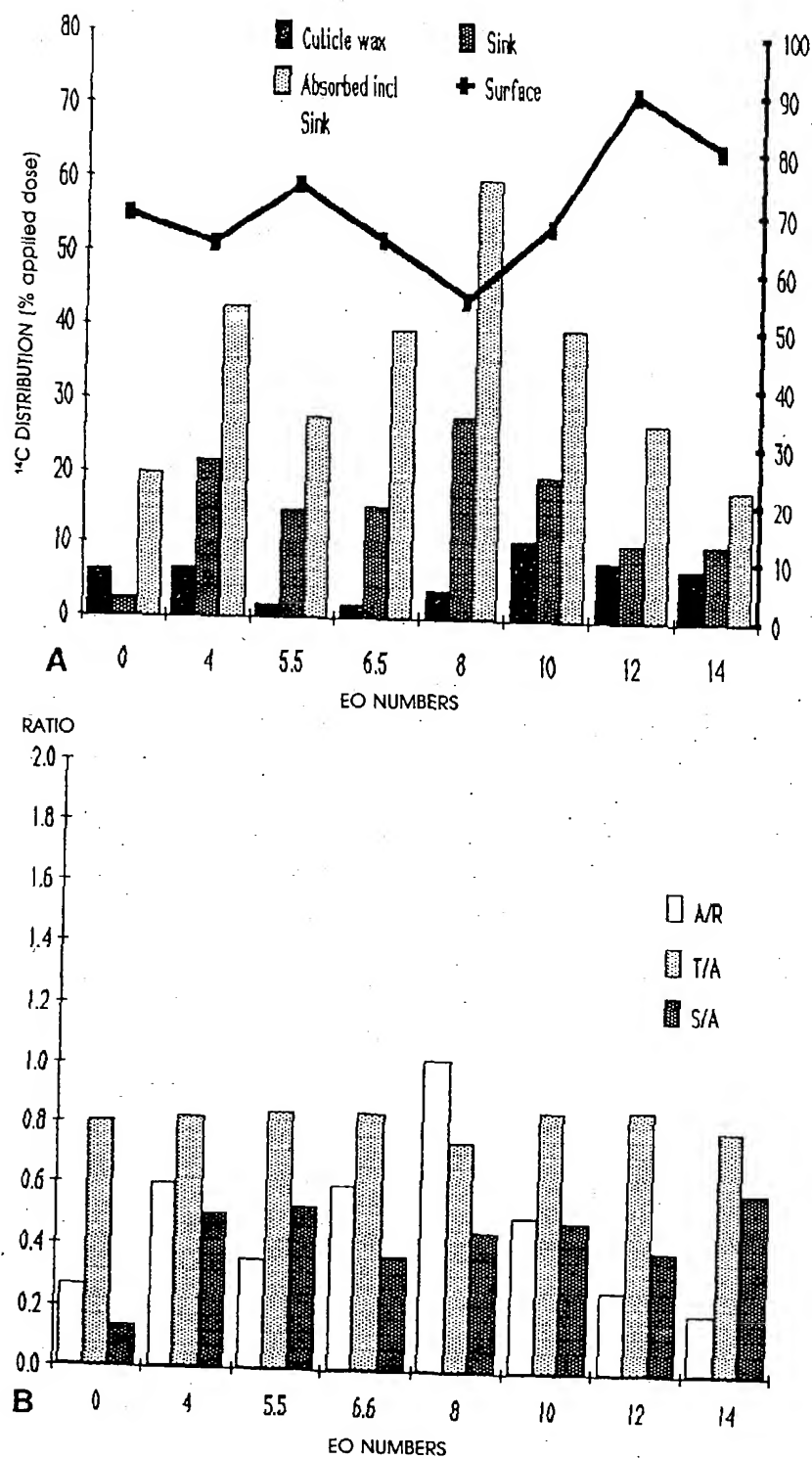


FIGURE 1. The effect of ethylan surfactants (EO 4 to 14) on the distribution of  $^{14}\text{C}$ -asulam applied to brackenfern. (A) Percent of applied dose; (B) absorption to surface residues (A/R), translocation to absorption (T/A), and sink accumulation/absorption (S/A) ratios.



In the case of  $^{14}\text{C}$ -diflufenican applied to bracken fern, incorporation of ethylan surfactants was beneficial to absorption and translocation only at EO 4 (Figure 2A). As EO increased, a marked rise in surface residues was coincident with a gradual reduction in cuticle wax levels and in uptake/movement. The decline in the ratios of S/A and particularly A/R confirm that only surfactant of low EO has a beneficial effect on the uptake and translocation of this lipophilic herbicide; T/A was unaffected by surfactant EO level (Figure 2B).

The effect of the surfactants on absorption and translocation of  $^{14}\text{C}$ -asulam by common chickweed is shown in Figures 3A and B. Absorption, but not translocation, was significantly increased by ethylans of EO 4 to 10, with an optimum of EO 6.5 to 8, surface residues of  $^{14}\text{C}$ -asulam being reduced proportionately; the low level of translocation was little affected by EO level. Ethylan surfactants had no significant effect on the uptake and transport of  $^{14}\text{C}$ -diflufenican, although cuticle wax retention was significantly reduced at EO 6.5 (Figure 4A). The A/R and T/A ratios indicate that absorption and especially translocation declined at the higher EO numbers (Figure 4B).

#### IV. DISCUSSION

The results presented here indicate that in brackenfern and to a lesser extent common chickweed, the nonylphenol surfactants tested do selectively stimulate the uptake and translocation of asulam and diflufenican. The uptake of asulam, which is relatively hydrophilic, was enhanced by surfactants of low to medium chain length, particularly around EO 8.0; the absorption of lipophilic diflufenican, however, was increased only by surfactant of EO 4, the most lipophilic of the test adjuvants.

These results tend to confirm the findings of Stevens and Bukovac,<sup>9</sup> who examined the uptake of 2-deoxy-D-glucose, atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane], which have water solubilities of about  $50 \text{ g l}^{-1}$ ,  $40 \text{ mg l}^{-1}$ , and  $17 \text{ g l}^{-1}$ , respectively. Uptake of glucose was directly related to the water content of the surfactants at 80% RH, and this content increased with both RH and the log EO content of the surfactant. They believed that the surfactants enhanced the uptake of 2D-glucose by maintaining the chemical in solution on the leaf surface, and found evidence to indicate that phytotoxic adjuvants (low EO) do not necessarily enhance uptake of glucose, unlike DDT or atrazine. These workers showed that uptake of these lipophilic compounds increased with the uptake of the surfactants, being inversely related to their hydrophile-lipophile balance (HLB). They suggested that the increased uptake of atrazine and DDT may have been associated with copenetration of the surfactants. It is noteworthy that the water solubilities of these relatively lipophilic compounds were increased up to eightfold by surfactants, particularly at intermediate HLBs. They concluded that surfactants with short EO chains would be adjuvants of choice to maximize the uptake of compounds of nonpolar active ingredients, while those with long EO chains would be preferable for water-soluble active ingredients.

In the present study, the incorporation of ethylan surfactants having a relatively high number of EO groups (asulam,  $>10$ ; diflufenican,  $>5.5$ ) generally was counterproductive, since the surface residues of herbicide increased markedly and the levels of absorption and translocation diminished. The partitioning of  $^{14}\text{C}$ -diflufenican into the cuticle waxes was also reduced in the presence of these surfactants, and it may be conjectured that this step reflects an initial rate-limiting phase in the process of cuticle penetration.

Comparison of the efficiency of uptake (percent of applied dose) indicates that for asulam in brackenfern, there was little relationship between uptake and the levels of  $^{14}\text{C}$  detected

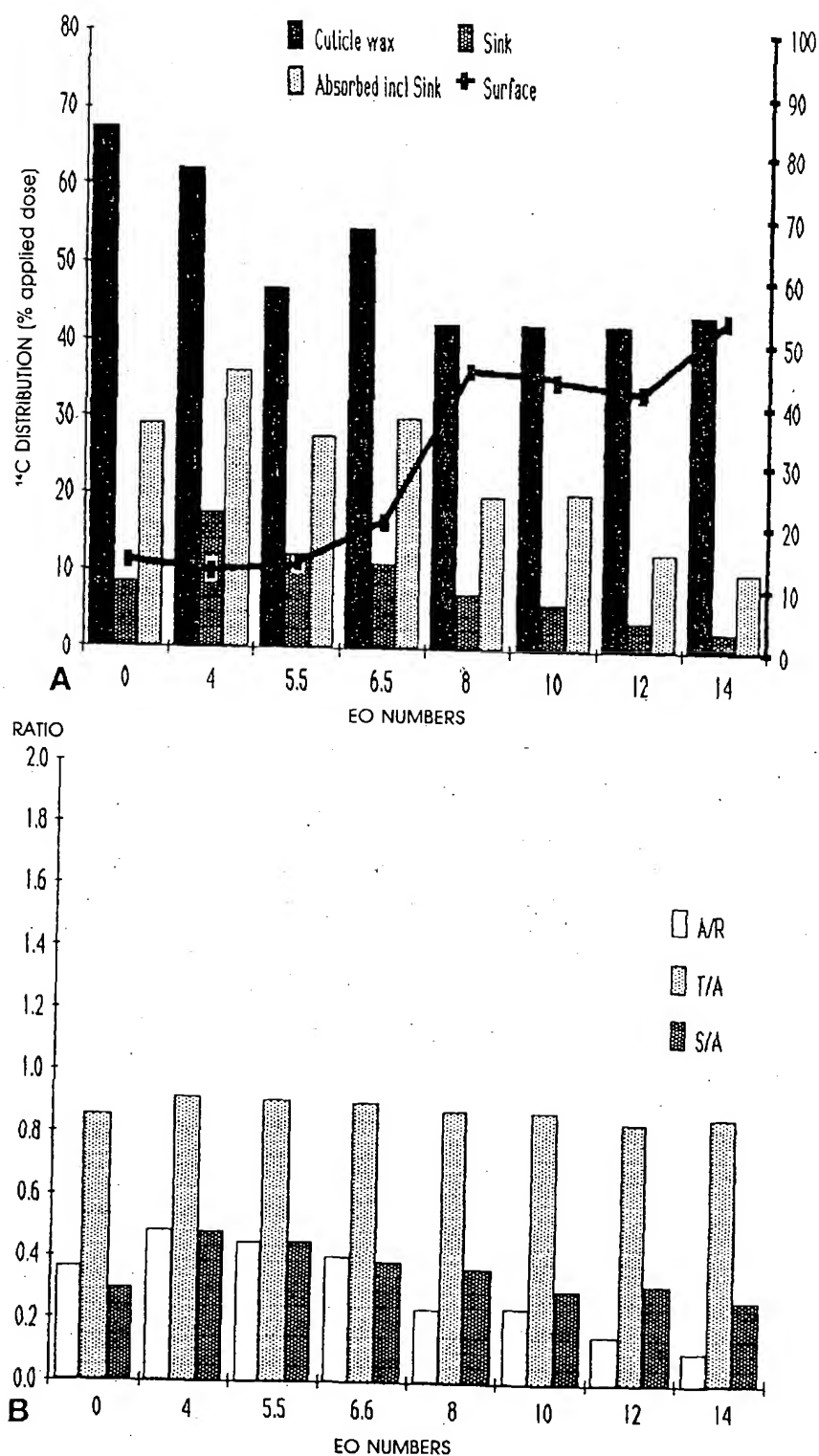
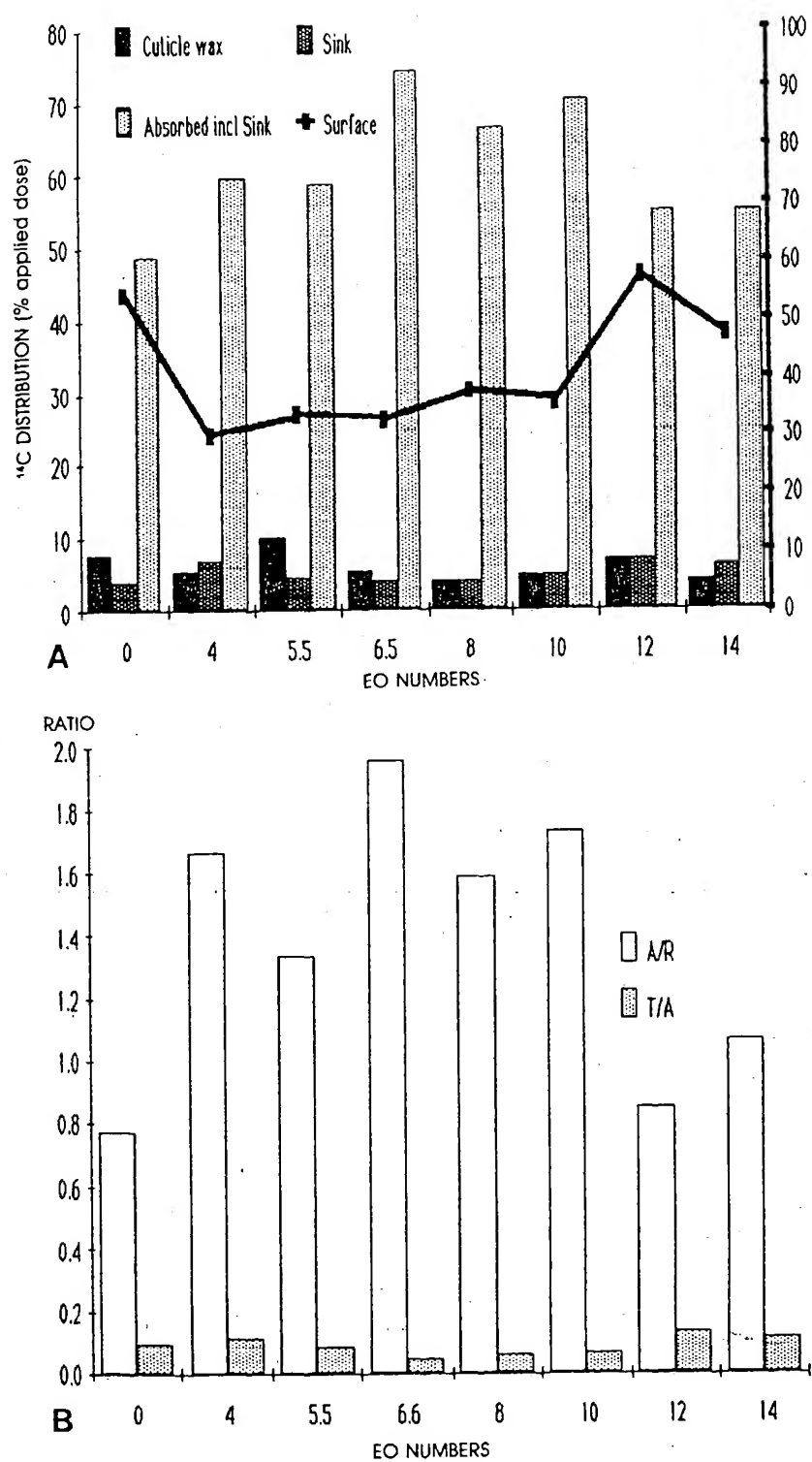


FIGURE 2. The effect of ethylal surfactants (EO 4 to 14) on the distribution of  $^{14}\text{C}$ -diflufenican applied to brackenfern. (A) Percent of applied dose; (B) as ratios of A/R, T/A and S/A.



**FIGURE 3.** The effect of ethylan surfactants (EO 4 to 14) on the distribution of  $^{14}\text{C}$ -asulam applied to common chickweed. (A) Percent of applied dose; (B) as ratios of A/R and T/A.

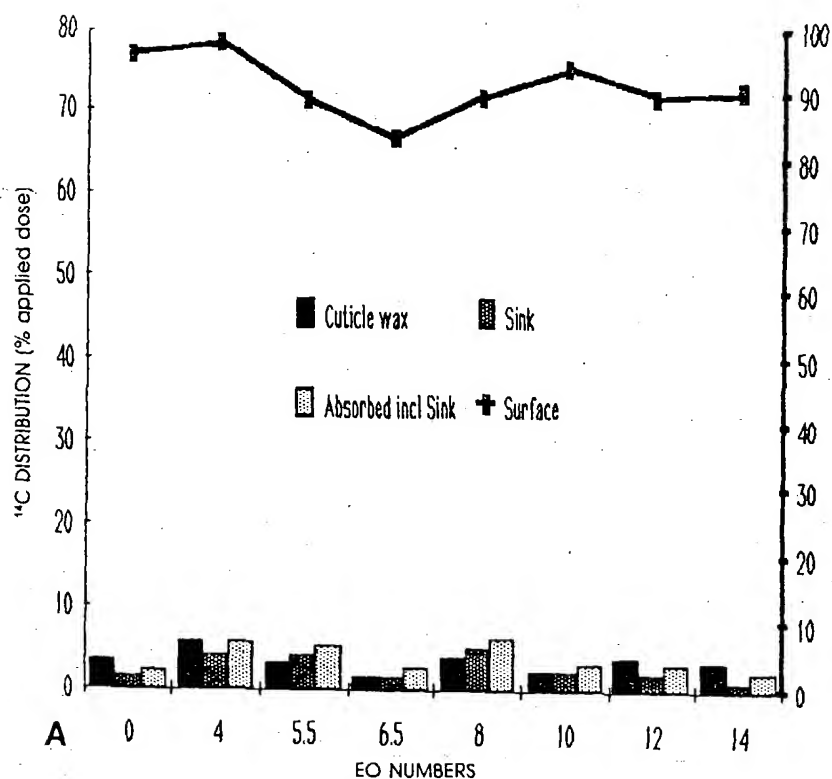


FIGURE 4. The effect of ethyl surfactants (EO 4 to 14) on the distribution of  $^{14}\text{C}$ -diflufenican applied to common chickweed. (A) Percent of applied dose; and (B) as ratios of A/R and T/A.

in the waxes. It may be that the flux of transport across the waxes is relatively low and that a relatively more hydrophilic pathway is involved which avoids the waxes. In the case of diflufenican, however, uptake and distribution in the waxes tended to be parallel, with the exception of EO 4. It could be conjectured that partitioning into the waxes may be an initial stage in cuticle penetration and that a lipid route was involved. Surfactant EO levels above 4.0 appeared increasingly to inhibit the efficiency of both processes.

In the case of  $^{14}\text{C}$ -asulam, the existence of an optimum of about EO 8.0 may reflect the need for an optimum HLB. An element of lipophilicity presumably enhances penetration of the cuticle membrane and absorption through the plasmalemma, while an appropriate hydrophilicity would help to maintain the chemical in solution on the surface and ensure effective partitioning into the aqueous phase in the inner regions of the cuticle membrane. Asulam is phloem systemic, and previous studies have indicated that the primary effect of nonionic surfactants such as Silwet® L-77 is associated with absorption, while the effects on phloem transport are secondary.<sup>3</sup>

The evidence presented in Figures 1A and 2A indicates that translocation of both compounds mirrors absorption; transport mechanisms per se appear to be largely unaffected. Calculation of the ratios of translocation or sink accumulation to absorption, however, indicates that in brackenfern, the relative sink accumulation of  $^{14}\text{C}$ -asulam was increased in the presence of all surfactants. It is known that nonionic surfactants can penetrate the leaf tissues,<sup>8</sup> possibly resulting in enhanced membrane permeability and short-distance transport of phloem-systemic, relatively low phytotoxic compounds, such as asulam.<sup>3</sup>

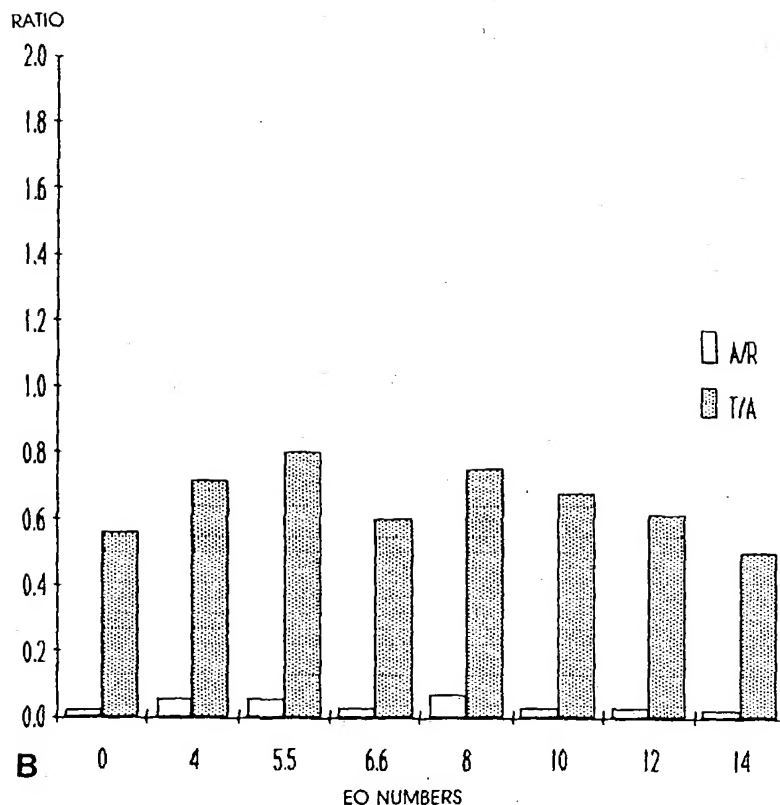


FIGURE 4 (continued).

While a high proportion was present in the cuticle waxes, especially at higher EO levels, the uptake (dpm) of diflufenican was greater than that of asulam. Translocation of the asulam, however, was considerably greater than that of diflufenican, particularly at EO 8, indicating that for effective absorption and phloem translocation, a foliage-applied herbicide requires a suitable HLB. It must be sufficiently lipophilic for cuticle and membrane penetration to occur, and it must be sufficiently hydrophilic to enable partitioning into the aqueous phase in which transport occurs. The importance of HLB has been discussed by Edgington<sup>2</sup> in relation to systemic fungicides. He emphasized that the permeability of nonionized compounds (such as asulam and diflufenican) should be sufficient to enable them to penetrate the phloem, but not so great that loss from the phloem would occur during translocation. Bromilow et al.<sup>1</sup> assessed the retention of a series of chemicals having varying octan-1-ol/ $H_2O$  partition coefficients ( $\log K_{ow}$ ) in the phloem and found that compounds with  $\log K_{ow}$  0 to 5 had a high retention, while those with values of  $<1.0$  were poorly retained. The results of the present studies are consistent with these findings, since the  $\log K_{ow}$  for asulam is 0.3, while that for diflufenican is 4.9.

The beneficial effect of these nonionic surfactants lies in improved uptake, with any effects on translocation being secondary. The mechanisms by which cuticle penetration of diflufenican (lipophilic) is enhanced by EO 4 surfactants (lipophilic) is unknown. It may be conjectured, however, that this surfactant enhances partition of this herbicide into, and possibly out of, the cuticular waxes. Retention in the waxes appears to be minimized at EO



4, unlike the situation at higher EO numbers. Enhanced water solubility of diflufenican by surfactants of higher EO number does not appear to be beneficial. In the case of asulam, the role of surfactants of EO 6.5 to 8.0 is uncertain, but they may improve the HLB of asulam, thereby facilitating transcuticle or transmembrane transport. The underlying explanations of these findings will be investigated further.

### ACKNOWLEDGMENTS

Appreciation is expressed in the British Council and the Royal Society of Edinburgh for financial support to Professor Chandrasena, enabling this study to be carried out. Grateful thanks are due to Rhone Poulenc for the gift of  $^{14}\text{C}$ -asulam and  $^{14}\text{C}$ -diflufenican, and to Dr. A. H. Catchpole of Rhone Poulenc for helpful comments. Grateful thanks are expressed to Mrs. Sheila McMillan for preparation of this manuscript.

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INFLUENCE OF ETHYLAN AND AMMONIUM SULFATE ON  
GLYPHOSATE PHYTOTOXICITY TO QUACKGRASS  
(*Elytrigia repens*)

Gilles D. Leroux and Gilles Hamel

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## ABSTRACT

In greenhouse experiments, additions of 0.5% (v/v) ethylan or 5.0% (w/v) ammonium sulfate increased the permeability of quackgrass (*Elytrigia repens*) leaf-cell membrane treated with a solution containing 250 mg l<sup>-1</sup> of technical-grade glyphosate-isopropylamine salt (MON 0139) [*N*-(phosphonomethyl)glycine] or formulated Roundup® (hereafter, glyphosate). Permeability reached a plateau at different times, depending upon the treatment. Rhizome bud viability was bioassayed using a 0.1% solution of 2,3,5-triphenyl tetrazolium chloride. Mean bud viability was reduced more by glyphosate than MON 0139, regardless of the concentrations (250, 750, and 1250 mg l<sup>-1</sup>). All treated and untreated plants had increasing bud viability with increasing distance from the treated shoot, but the viability in untreated plants and those treated with 250 mg l<sup>-1</sup> MON 0139 increased at a greater rate than the ones treated with glyphosate with increasing distance from the treated shoot. Additions of 0.5% (v/v) ethylan or 5.0% (w/v) ammonium sulfate increased by about 25% the phytotoxicity to quackgrass of sprays containing 250 mg l<sup>-1</sup> glyphosate. Neither adjuvant modified the distribution of glyphosate in rhizomes, compared to glyphosate alone, but rhizome growth subsequent to glyphosate treatment was less with the addition of ammonium sulfate or ethylan than with glyphosate alone.

## I. INTRODUCTION

Quackgrass is a persistent perennial grassy weed that infests most crops of humid temperate climate.<sup>18</sup> Effective quackgrass control was made possible with the advent of systemic herbicides able to reach rhizome buds in lethal concentration. Glyphosate, a post-emergence, nonselective, systemic herbicide, has been shown to be highly effective against quackgrass,<sup>3,12,14</sup> but high rates are expensive and long-term control may not be obtained with low rates due to inadequate killing of rhizome buds.

Adjuvants include inorganic salts and surfactants that are added to herbicides to improve their efficiencies. The use of surfactants as adjuvants to enhance herbicide activity has been well documented for several herbicides. About 50 years ago, ammonium sulfate (AMS) was used to activate dinitro-*o*-cresol herbicide, DNOC.<sup>4,7</sup> More recently, it was shown that AMS can activate several water-soluble leaf-applied herbicides, including glyphosate.<sup>16,19</sup> Blair<sup>1</sup> has shown that AMS increases the phytotoxicity of glyphosate to quackgrass. In the U.K., the half-dose (0.72 of acid equivalent (a.e.) per hectare) had almost as much effect as the full dose of glyphosate.<sup>8</sup> Occasionally, marked increases in activity were observed when AMS (50 g l<sup>-1</sup>) was added to the spray solution.<sup>17</sup>

The cationic surfactant Frigate® (fatty amine ethoxylate; hereafter, ethylan) has been found to enhance the activity of the commercial formulation of glyphosate and is recommended for use.<sup>16</sup> Evidence exists that surfactants increase spray retention and subsequent penetration of leaves by herbicides. Surfactants may also solubilize the waxy cuticles of plants, thereby facilitating herbicide entry.

To determine whether leaf cell membrane is altered, inorganic salt leakage from foliar tissues can be measured by incubating them in herbicide solution with adjuvant, in comparison to the herbicide itself and distilled water.<sup>11</sup> Adjuvants applied to plant foliage can change the integrity of the leaf-cell membrane. Increased permeability of the leaf-cell membrane may explain why adjuvants give greater penetration and subsequent translocation of herbicides in plants.

Indirect methods to bioassay the viability of vegetative buds include germination tests in soil,<sup>3,9</sup> agar,<sup>10</sup> and water-saturated substrates.<sup>2</sup> These methods detect only those buds that

have the immediate potential to grow, not those that are dormant.<sup>5</sup> The respiratory activity of cells can be directly evaluated by using triphenyl tetrazolium chloride.<sup>13</sup> This method has the advantage of assessing the viability of both dormant and nondormant quackgrass rhizome buds.<sup>5,15</sup>

The objectives of the study were to (1) compare the influence of formulated Roundup® (glyphosate) to that of technical glyphosate isopropylamine salt (MON 0139), with or without AMS or ethylan, on leaf-cell membrane permeability of quackgrass, (2) compare the effects of increasing rates of glyphosate to those of MON 0139 on quackgrass bud viability, and (3) evaluate the effects of AMS and ethylan on quackgrass rhizome bud viability as affected by increasing rates of glyphosate.

## II. MATERIALS AND METHODS

Quackgrass (Laval University clone no. 2) was propagated in the greenhouse (16-h photoperiod;  $20 \pm 3^\circ\text{C}$ ; RH, 45% by planting three-bud rhizome segments in 17-cm pots filled with potting mix consisting of peat moss, decomposed organic soil, sand, vermiculite, and perlite (2:2:2:1:1, v/v/v/v/v). Plants were irrigated twice a day and fertilized weekly with 100 ml of 20-20-20 at  $4 \text{ g l}^{-1}$ .

### A. EXPERIMENT 1

When quackgrass plants reached the six-leaf stage, 15 foliar discs (5-mm diameter) from the second-oldest leaf were placed in a 60-ml test tube with 5 ml of treatment solution. The electrical conductivity of the solution was monitored at various intervals over a 48-h period with a Copenhagen conductivity meter. There were nine treatments: formulated glyphosate and MON 0139 (an isopropylamine salt formulation of glyphosate without wetter), each used at  $250 \text{ mg a.e. l}^{-1}$ , ethylan at 0.5% (v/v), AMS at 5.0% (w/v), and combinations of glyphosate or MON 0139 with or without ethylan or AMS. Distilled water was used as an untreated control. Variation in conductivity was assumed to result from solute leakage from leaf discs.

### B. EXPERIMENT 2

The influence of increasing rates of glyphosate or MON 0139 on bud viability was studied. Plants were propagated as above. The first emerging shoot was identified as the primary stem. The plants were grown for 40 d in the greenhouse. Before treating the plants, the number and position of buds on the primary rhizome were mapped, and the length of the rhizome was measured. The primary aerial stem was dipped for 30 s in herbicide solution containing 0, 250, 750, and  $1250 \text{ mg a.e. l}^{-1}$  of either glyphosate or MON 0139. The plants were allowed to dry in a horizontal position to ensure that no herbicide contacted the soil. After treatments, plants were returned to the greenhouse for 6 d. The growth increment of the primary rhizomes was measured after excavating the plants. Bud viability was then bioassayed with 0.1% (w/v) of 2,3,5-triphenyl tetrazolium chloride.<sup>15</sup> The rhizomes were cut into sections containing one bud. Bud viability was visually evaluated by using a color index with 1 (white) corresponding to no viability and 5 (purple) to 100% viability. The results are reported as a percentage of the untreated control.

### C. EXPERIMENT 3

The effect of ethylan and AMS added to glyphosate on quackgrass bud viability was assessed. The rate of herbicide used was  $250 \text{ mg a.e. l}^{-1}$ . Ethylan and AMS were used at 0.5% (v/v) and 5.0% (w/v), respectively. The same procedure as above was followed.

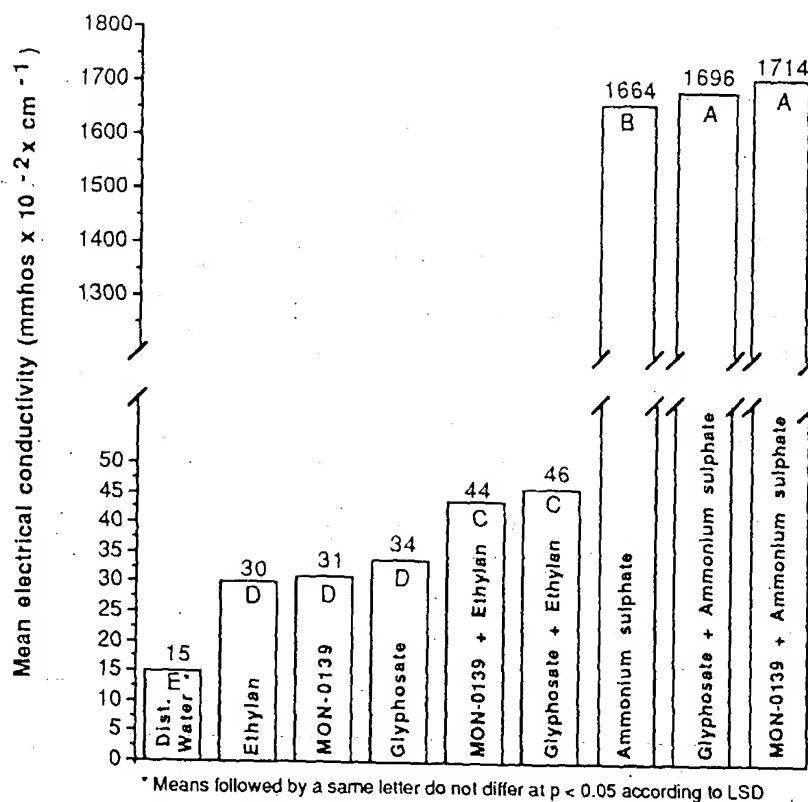


FIGURE 1. Effects on mean leaf-cell membrane permeability of ethylan and AMS added to glyphosate or MON 0139.

Each experiment used a completely randomized design with four replications. Each experiment was repeated twice and the data was submitted to standard analysis of variance after testing for homogeneity of variance. Treatment means were compared at  $p \leq 0.05$  with the LSD (least significant difference) test. Regression analyses were performed to assess the influence of bud position on the response to herbicide treatments.

### III. RESULTS AND DISCUSSION

#### A. EXPERIMENT 1

The addition of ethylan to either glyphosate or MON 0139 increased ( $p < 0.05$ ) the mean leaf-cell permeability over that of glyphosate or MON 0139 (Figure 1). Mean leaf-cell permeability was increased severalfold by AMS over that of any other treatments. AMS increased the leaf-cell permeability of foliar discs treated with glyphosate and MON 0139. Any treatment resulted in greater leaf-cell permeability than the distilled water control.

Prendeville and Warren<sup>11</sup> have shown no effect of glyphosate on the leaf-cell permeability of bean (*Phaseolus vulgaris* L.) and soybean (*Glycine max* L. [Merr.]) up to 12 h after treatment. They used a different procedure, but the rate of glyphosate used was similar. Plants were sprayed "to run off" and discs were punched from the leaves at different intervals, rinsed with, and incubated in distilled water. Conductivity of the ambient solution was then measured. While this procedure has the advantage of providing a common basis

for treatment comparison, it necessitates rinsing which results in solute leakage that is not taken into account in measurements.

The leaf-cell permeability reached a plateau about 4 h after treatment when no adjuvant was used with any of the herbicides (Figure 2). The permeability was constantly greater with glyphosate than with MON 0139. The mean electrical conductivity for foliar discs treated with herbicides was about twice that for untreated discs. The addition of ethylan to either herbicide increased the leaf-cell permeability, with a plateau at 16 h after treatment. The leaf-cell permeability reached a maximum (nearly  $50 \text{ mmhos} \times 10^{-2} \text{ cm}^{-1}$ ) at 32 h after treatment for a mixture of any herbicide with ethylan, compared to 48 h with herbicide alone (nearly  $40 \text{ mmhos} \times 10^{-2} \text{ cm}^{-1}$ ). These results indicate that ethylan increases the rate of herbicide penetration compared to herbicide alone.

The addition of AMS increased by about 50-fold the leaf-cell permeability of glyphosate and MON 0139. The leaf-cell permeability reached a plateau at 4 h for AMS and MON 0139 + AMS, and at 6 h for glyphosate + AMS (Figure 2). The leaf-cell permeability of foliar discs treated with MON 0139 was greater than that of discs treated with glyphosate. About 12 h after treatment, there was a steady decline in leaf-cell permeability when AMS was used. Growers have often noticed the rapid phytotoxic response of plants treated with glyphosate + AMS, but our results do not indicate any marked difference between treatments including AMS.

## B. EXPERIMENT 2

Glyphosate reduced the mean bud viability of quackgrass rhizome to a greater extent than did MON 0139 (Table 1). The viability of glyphosate-treated buds was constantly less than that of those treated with MON 0139, regardless of the rate (Table 2). This result points out the usefulness of the surfactant added to the commercial formulation.

The position of buds on the rhizome had a marked effect on its viability following treatment (Figure 3). In all cases, herbicide-treated and untreated plants had increasing viability with increasing distance from the treated shoots. This result has been reported in the literature,<sup>5,15</sup> but the viability in untreated plants and those treated with  $750 \text{ mg l}^{-1}$  of MON 0139 increased at a greater rate than in those treated with glyphosate, with increasing distance from the treated shoot. While viability was lower than the 3.5 index value for all bud positions with glyphosate, the bud viability exceeded that value for bud positions greater than 5 and 7 of untreated- and MON 0139-treated plants, respectively. The best-fit regression equations for bud viability (Y) in relation to bud position (B) are presented in Figure 3 for the  $750 \text{ mg l}^{-1}$  glyphosate treatment. The coefficients of determination  $R^2$  ( $p \leq 0.001$ ) varied between 0.71 and 0.84. Similar regression equations were obtained at 250 and  $1250 \text{ mg l}^{-1}$  rates (data not shown).

## C. EXPERIMENT 3

The addition of ethylan or AMS increased by about 25% the phytotoxicity to quackgrass of solutions containing  $250 \text{ mg l}^{-1}$  of glyphosate (Table 3). Compared to the untreated control, the viability of glyphosate-treated buds averaged over 87%. In previous work, we have shown that no difference existed between glyphosate-treated and untreated buds when using tetrazolium for testing the viability of five quackgrass biotypes.<sup>12</sup> In contrast, bud viability was significantly reduced by glyphosate when buds were allowed to germinate on an agar medium. Great care should be taken when comparing the two methods. While the germination response to herbicide treatments may be more readily detected, total kill of the buds, as evaluated by using tetrazolium chloride, is not completed at the time of appraisal. Some studies have shown that  $^{14}\text{C}$ -glyphosate tends to accumulate in the apical portion of quackgrass rhizomes.<sup>3,6</sup> Our results indicate that bud viability increased as buds were po-



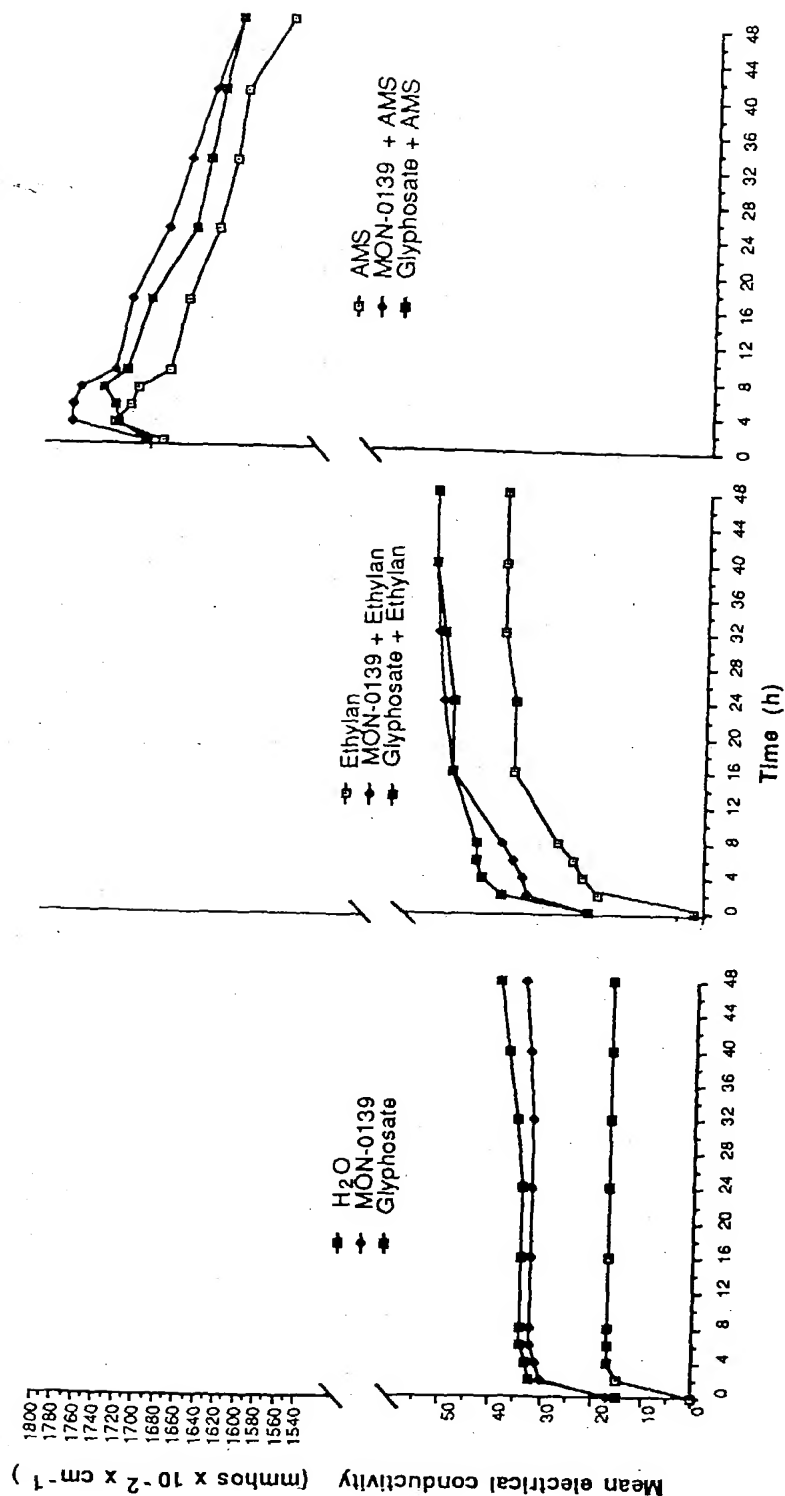


FIGURE 2. Time course of leaf-cell membrane permeability as influenced by ethylal and AMS added to glyphosate or MON 0139.



TABLE 1  
Effect of MON 0139 and  
Glyphosate on Mean  
Quackgrass Bud Viability

Treatment	Mean bud viability (% of control)
MON 0139	88.1 a
Glyphosate	59.7 b

Note: Means followed by the same letter do not differ at  $p < 0.05$  according to LSD.

TABLE 2  
Dose Response of Quackgrass  
Bud Viability to MON 0139  
and Glyphosate

Rate of a.e. (mg l <sup>-1</sup> w/v)	Glyphosate	MON 0139
	(% of control)	
0	100 a	100 a
250	61 b	105 a
750	44 c	70 b
1250	47 c	67 b

Note: Means followed by the same letter do not differ at  $p < 0.05$  according to LSD.

sitioned near the apex (Figure 3). While this may seem contradictory, glyphosate may accumulate in the apex and stimulate the respiratory activity of bud tissues, thus depleting their nutritive reserve at a faster rate. With time, a greater rate of kill is achieved in the apex of the rhizome rather than in the basal part.

Neither adjuvant modified the distribution of glyphosate among the rhizome buds, as reflected by a similar pattern of bud viability response (data not shown), but rhizome growth subsequent to glyphosate treatment was less with adjuvants than with glyphosate or no herbicide (Table 4). These results confirm those of Turner and Loader,<sup>16</sup> who have shown that both ethylan and AMS increased the phytotoxicity of glyphosate to quackgrass.

It is evident from our study that glyphosate modifies the leaf-cell permeability of quackgrass. Both adjuvants used have enhanced the penetration of glyphosate, thus favoring translocation toward the rhizomes. In general, glyphosate penetration was prolonged in the presence of an adjuvant, as solute leakage reached a plateau at a later stage than in the absence of an adjuvant. As a result, the growth increment following treatment with glyphosate was inferior when adjuvants were added to the herbicide solution. The usefulness of the adjuvant added to formulated glyphosate was demonstrated by a greater reduction of bud viability compared to unformulated glyphosate (MON 0139).

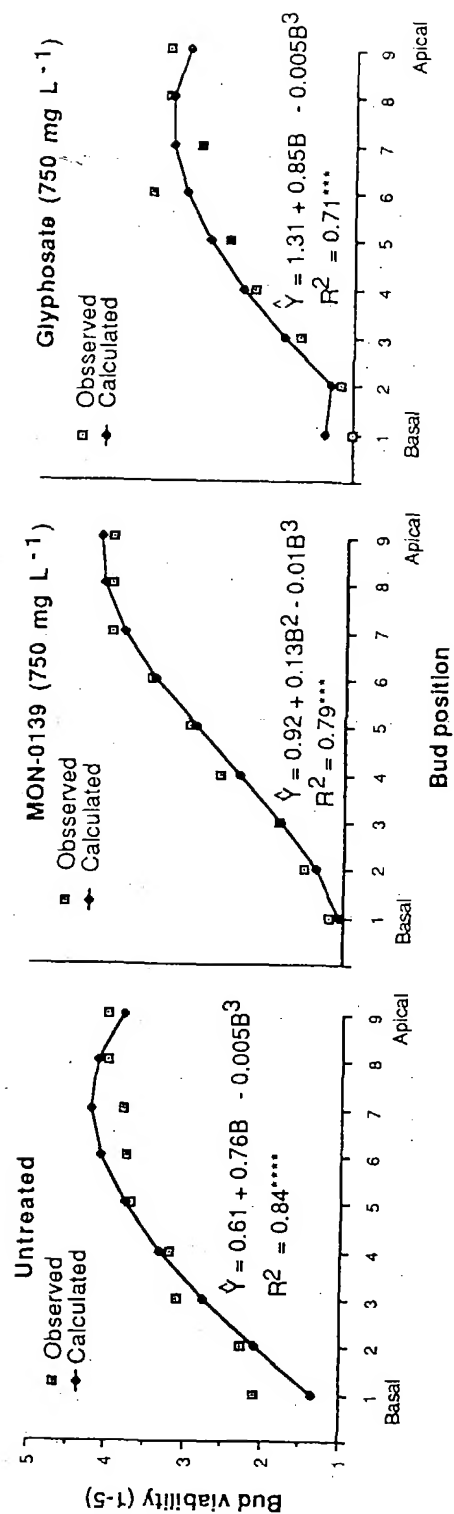


FIGURE 3. Effects of glyphosate and MON 0139 on bud viability as influenced by position on rhizome.

TABLE 3  
Effect on Mean Bud Viability of  
Adding Ethylan or AMS to Glyphosate  
Applied at 250 mg l<sup>-1</sup>

Treatment	Mean bud viability (% of control)
Glyphosate	87.5 a
Glyphosate + ethylan	66.0 b
Glyphosate + AMS	63.2 b

Note: Means followed by the same letter do not differ at  $p < 0.05$  according to LSD.

TABLE 4  
Effect on Rhizome Growth  
Increment after Adding Ethylan  
or AMS to Glyphosate Applied  
at 250 mg l<sup>-1</sup>

Treatment	Rhizome growth (cm)
Control	7.64 a
Glyphosate	6.41 a
Glyphosate + ethylan	4.27 b
Glyphosate + AMS	2.62 b

Note: Means followed by the same letter do not differ at  $p < 0.05$  according to LSD.

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## Chapter 11

INFLUENCE OF ADJUVANTS ON CUTICULAR PENETRATION  
AND METABOLISM OF AMINOCARB FOLLOWING TOPICAL  
APPLICATION OF MATACIL® 180F FORMULATIONS TO  
SPRUCE BUDWORM

Kanth M. S. Sundaram

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## ABSTRACT

Three mixtures, AID-585, AS-7N, and AA-3409, were prepared by mixing Matacil® 180F (a commercial formulation of aminocarb) with a light oil (insecticide diluent, ID 585), a heavy oil (Sunspray® 7N) or a surfactant (Atlox® 3409F)/water, respectively. The mixtures were fortified with  $^{14}\text{C}$ -ring labeled aminocarb and were topically applied to fifth instar larvae of the spruce budworm. Penetration rates and depletion of the external residues were determined by  $^{14}\text{C}$ -assay. The amount of aminocarb penetrated into the insects was determined by macerating them and extracting with ethyl acetate. The parent material and its metabolites present in the external rinses and in the extracts were determined by thin-layer-chromatography and a liquid scintillation counter. Penetration rates of aminocarb in the three mixtures varied according to the type of adjuvants present in them. The increasing order of penetration was AID-585 > AS-7N > AA-3409. The metabolites found, in decreasing order of concentration, were 4-methylamino, 4-amino, and 4-methylformamido aminocarbs. Trace levels of 4-formamido aminocarb, and 4-dimethylamino and 4-methylamino 3-methylphenols, were tentatively identified. The amount of aminocarb and its metabolites found varied according to the type of adjuvants and the rate of penetration.

## I. INTRODUCTION

Aerial application of insecticides to control spruce budworm, *Choristoneura fumiferana* (Clem.), a widely distributed and most destructive defoliator of coniferous forests in eastern North America, is a well-established pest management strategy in Canada.<sup>13</sup> Aminocarb (trade name, Matacil®, 4-dimethylamino-3-methylphenyl *N*-methylcarbamate), a broad-spectrum contact insecticide, has been used since 1970 to control budworm populations in forests.<sup>16</sup> It is hypothesized that the mode of entry of sprayed toxicant is either due to (1) direct impingement of droplets on insects, (2) indirect contact with contaminated webbing within the microhabitat, or (3) ingestion of contaminated needles by budworm.<sup>9</sup>

Aminocarb kills budworm by virtue of being a cholinesterase inhibitor.<sup>2</sup> Topical application of the chemical showed that it is extremely toxic to insects.<sup>15</sup> It is postulated<sup>3</sup> that contact insecticides generally spread over the insect cuticle, enter the insect by crossing the integument, dissolve in the hemolymph, and eventually cause death. Assuming that penetration through the integument is the mechanism of entry of aminocarb into the insect, it is not yet clear (1) whether the penetration rate is influenced by the adjuvants present in different forestry spray mixes and (2) how rapidly the penetrated and surface residues are degraded in the insect. The toxicity of various aminocarb spray mixes is not only a function of the active ingredient (a.i.), but also of the adjuvants present in them.<sup>7,8,20</sup> Therefore, this study was undertaken with two objectives in mind: (1) to determine the effect of adjuvants on the cuticular penetration of topically applied aminocarb in fifth-instar budworm larvae and (2) to study the *in vivo* degradation and metabolism of the chemical in the insect.

## II. MATERIALS AND METHODS

### A. CHEMICALS

The radioactive aminocarb labeled with  $^{14}\text{C}$  in the aryl ring ( $^{14}\text{C}_{\text{Ar-O-}}$ ) (specific activity 11.7 mCi/mmol and >99% purity), analytical-grade aminocarb and its metabolites (purity >97%) listed in Table 1 were supplied by Mobay Chemical Corp., Kansas City, MO.

All organic solvents used were pesticide grade from Caledon, Georgetown, Ontario, Canada. The scintillation cocktail (Instal-Gel®) and the  $^{14}\text{CO}_2$  absorber (Carbosorb®) were obtained from United Technology Packard. Anhydrous sodium sulfate (Fisher) was heated overnight at 260°C prior to use.



**TABLE 1**  
**Aminocarb and Some of Its Metabolites Found in Spruce Budworm Rinses and Homogenates with Their Structural Formulas and Corresponding  $R_f$  Values in Isopropyl Ether: Acetonitrile (4:1, v/v) Solvent System**

NAME	STRUCTURAL FORMULA	ABBREVIATION	$R_f$
4- Dimethylamino-3-methylphenyl N-methylcarbamate		A	0.75
4- Methylformamido-3-methylphenyl N-methylcarbamate		MFA	0.24
4- Methylamino-3-methylphenyl N-methylcarbamate		MAA	0.64
4- Formamido-3-methylphenyl N-methylcarbamate		FA	0.20
4- Amino-3-methylphenyl N-methylcarbamate		AA	0.41
4- Dimethylamino-3-methylphenol		DAP	0.81
4- Methylamino-3-methylphenol		MAP	0.79

## B. FORMULATIONS

The three formulations used in the study along with their abbreviations, compositions, and some key physical properties are given in Table 2. The suppliers of the formulation components are given in the footnotes. The Matacil® 180F formulations; AID-585 (oil solution), and AA-3409 (aqueous emulsion) are currently registered for forestry use in Canada, whereas the experimental formulation AS-7N (oil suspension) is prepared from the oil-soluble concentrate, Matacil® 1.8D (which is currently phased out), containing nonyl-phenol.

A 1-ml aliquot of each formulation was prepared in volumetric flasks by mixing the required amount of the ingredients listed in Table 2, using either micropipettes or burettes. A standard stock solution of  $^{14}\text{C}$ -aminocarb (sp activity 11.7 mCi/mmol) in ethyl acetate containing 0.05 g/ml was prepared to give  $104 \times 10^3$  dps/50  $\mu\text{g}/\mu\text{l}$ . To each formulation, 100  $\mu\text{l}$  of the stock solution was added to give  $9.46 \times 10^3$  dps/ $\mu\text{l}$ . The total aminocarb (labeled 4.5  $\mu\text{g}/\mu\text{l}$  + unlabeled 47.4  $\mu\text{g}/\mu\text{l}$ ) concentration in the end-use formulation was 51.9  $\mu\text{g}/\mu\text{l}$ . The volumetric flasks containing the formulations were tightly capped and shaken thoroughly for uniform concentration. Each flask was wrapped in aluminum foil to minimize possible photolysis and stored at 0°C until use.

TABLE 2  
Composition (vol %) of Aminocarb (Matacil® 180 F) Formulations Used in the Study and Their Properties at 20°C

Formulation composition (vol %)	Abbreviation	Density (g/ml)	Viscosity (mPas · s)	Surface tension (mN/m)
Matacil® 180F <sup>a</sup> (26.7) + I.D. <sup>b</sup> 585 (73.3)	AID-585	0.837	4.00	29.1
Matacil 180F (26.7) + Sunspray®7N <sup>c</sup> (73.3)	AS-7N	0.884	30.5	31.1
Matacil 180F (26.7) + Atlox® 3409 <sup>d</sup> (1.3) + distilled water (72.0)	AA-3409	1.011	2.42	30.3

<sup>a</sup> Matacil® 180F (trade name for aminocarb [19.5% by weight] containing air-milled particles of a.i. at 2- to 3- $\mu$ m-diameter size suspended in oil) supplied by Chemagro Ltd., Mississauga, Ontario, Canada.

<sup>b</sup> I.D. insecticide diluent 585 — a refined light petroleum distillate supplied by Shell Canada Ltd. It distills at or below 308°C and is composed of alkylated benzenes and naphthalenes.<sup>5</sup>

<sup>c</sup> Sunspray®7N — a viscous, refined heavy petroleum distillate supplied by Sun Oil Co., Philadelphia, PA. It distills at about 410°C (30 mmHg) and is composed of paraffinic hydrocarbons.<sup>19</sup>

<sup>d</sup> Atlox® 3409F — alkene/aryl sulfonate emulsifier supplied by Atkemix, Inc., Brantford, Ontario, Canada.

### C. BUDWORM LARVAE

Budworm larvae were reared on an artificial diet at the Insect Production Unit of this institute and supplied to the study. Insects of uniform size (length,  $2.1 \pm 0.4$  cm; mass,  $0.012 \pm 0.005$  g) were selected and used in the experiment. Ten larvae per test and three replicates for each time period and formulation were used. When variability was large, more replicates were added.

### D. APPLICATION OF AMINOCARB

Each aminocarb formulation was applied topically to budworms using a calibrated B. D. Yale-G498 syringe attached to an ISCO-Microapplicator (Model M). Sets of ten insects were taken in Teflon® Oak Ridge\*-type centrifuge tubes (Nalgene cat. no. 3114-0010) and ten 1- $\mu$ l droplets of about 1250- $\mu$ m diameter were added to each set. The tubes were tightly sealed and shaken (Sybron Thermelyne Maxi Mix®) to ensure uniform coating of the chemical on the insects. During and after insecticide application, the larvae were kept in an environmental chamber maintained at  $15 \pm 1^\circ\text{C}$  and  $80 \pm 3\%$  relative humidity under simulated sunlight (400 W multivapor discharge lamps).

### E. EXTRACTION PROCEDURE

At 0, 15, 30, 45, 60, 90, 120, 150, and 180 min posttreatment, aminocarb remaining outside the insect was removed by washing the larvae in the centrifuge tube twice with 5 ml of ethyl acetate. The pooled washings were dried through a column of anhydrous sodium sulfate, evaporated under vacuum to a known volume, and aliquots used for liquid scintillation counter (LSC) and thin-layer chromatography (TLC).

Aminocarb that had penetrated into the insect was quantified by homogenizing the washed insects in a Sorvall Omni-Mixer® (DM-2000) with  $3 \times 5$  ml of acetonitrile and filtering under suction using a Millipore® filter. The pooled extract was passed through an anhydrous sodium sulfate column, concentrated under low pressure, and partitioned with 5 ml of hexane. The acetonitrile and hexane layers were gently flash evaporated to dryness and the residues taken in ethyl acetate for LSC and TLC studies.

\* Teflon is the registered trademark of E. I. du Pont de Nemours and Company, Inc., Wilmington, DE.

TABLE 3  
Penetration Rate and Percent Recovery of  $^{14}\text{C}$ -Activity in  
Different Budworm Fractions After Topical Application of  
 $^{14}\text{C}$ -Aminocarb Formulations

Time after application (min)	Average % activity in different fractions*				
	EtOAc rinse	$\text{CH}_3\text{CN}$ layer	Hexane layer	Bound $^{14}\text{C}$	Total
Formulation: AA-3409					
0	97	2	0.3	0.2	99.5
15	92	6	0.2	0.2	98.4
30	86	12	0.3	0.2	98.5
45	79	21	0.5	0.3	100.8
60	69	27	0.6	0.5	97.1
90	64	33	0.5	0.8	98.3
120	62	32	0.4	0.7	95.1
150	60	33	0.6	0.8	94.4
180	60	33	0.5	0.8	94.3
Formulation: AID-585					
0	90	10	0.2	0.0	100.2
15	70	29	0.1	0.2	99.3
30	52	47	0.3	0.2	99.5
45	44	53	0.2	0.3	97.5
60	30	64	0.2	0.2	94.4
90	27	65	0.3	0.3	92.6
120	27	66	0.3	0.4	93.7
150	25	65	0.2	0.3	90.5
180	24	64	0.3	0.4	88.7
Formulation: AS-7N					
0	93	7	0.2	0.0	100.2
15	81	17	0.3	0.0	98.3
30	70	28	0.2	0.0	98.2
45	61	38	0.2	0.2	99.4
60	49	48	0.4	0.3	97.7
90	46	51	0.2	0.2	97.4
120	47	50	0.4	0.3	97.7
150	44	52	0.3	0.2	96.5
180	45	50	0.3	0.4	95.7

\* Values represent the mean for three replicate measurements. Standard deviations were less than 15% (not shown).

The unextractable  $^{14}\text{C}$ -activity in the larval residue was estimated by combusting aliquots of it to  $^{14}\text{CO}_2$  in a Packard Oxidizer-306 and counting in the LSC after absorbing the gas in Carbosorb®.

#### F. RESOLUTION OF AMINOCARB AND ITS METABOLITES

Aminocarb and its metabolites in the ethyl acetate wash and the acetonitrile phase of the larval extract following hexane partition were separated and analyzed by TLC.<sup>18</sup> The hexane phase was discarded due to its low level of radioactivity (<1%, AA-3409, range 0.2 to 0.6%; AID-585, range 0.1 to 0.3%; AS-7N, range 0.2 to 0.4%) (Table 3). Baker's

Si-HPF-7011-4 chromatoplates coated with a sorbent layer (200  $\mu\text{m}$ ) containing a mixture of 5  $\mu\text{m}$   $\text{SiO}_2$  and 254 nm fluorescent indicator were used. Instead of the hexane-acetone (1:1, v/v) and diethyl ether-hexane-ethanol (77:20:3, v/v) solvent systems used earlier,<sup>18</sup> an isopropyl ether-acetonitrile (4:1, v/v) solvent system<sup>19</sup> was used in the present study to separate the parent material and its major metabolites (Table 1). Known nonradioactive compounds (Table 1) were chromatographed with aminocarb and its metabolites to help in identifying unknown products. The names of the compounds and their structural formulas, abbreviations, and  $R_f$  values obtained in this study are listed in Table 1. The fluorescent spots obtained for each compound on the chromatoplate were viewed under a UV lamp, and were further confirmed by radioautography.<sup>17</sup> The spots were carefully removed by scraping, transferred to scintillation vials containing Insta-Gel®, and the radioactivity determined with a Beckman LS-9000 liquid scintillation counter. The scrapings of the spots corresponding to all unidentified metabolites, including those remaining at the origin of the chromatoplate after solvent separation, were pooled, and its activity measured and recorded as unknown in Tables 4 and 5. No further attempts were made to either separate or identify the individual moieties present in them. The two phenols, DAP and MAP, were found in isolated cases and in very low amounts (about 0.5%) in the insect rinses (Table 4) and homogenates (Table 5). Their  $R_f$  values (Table 1) were very close and their individual quantification was not possible. Consequently, their combined activities, rather than their individual values, are recorded in Tables 4 and 5.

### III. RESULTS AND DISCUSSION

#### A. CUTICULAR PENETRATION OF $^{14}\text{C}$ -AMINOCARB

Rates of penetration for the three formulations, expressed as percent activity in the three solvent fractions, are given in Table 3. The dosages used in the study were manyfold higher than the  $\text{LD}_{50}$  value (1.3  $\mu\text{g}$  per insect for western spruce budworm, *Choristoneura occidentalis* Freeman),<sup>15</sup> which resulted in death of the insects within 20 to 25 min after application. The data (Table 3) clearly show the difference in the rate of penetration of radioactive aminocarb through the integument of the budworms. The formulation AID-585, containing ID 585 (low-boiling petroleum distillate composed of aromatics), penetrated most, and the formulation AS-7N, having less-volatile long-chain paraffinic hydrocarbons as solvent, penetrated moderately. In striking contrast, the emulsion formulation AA-3409 penetrated least. For AID-585, the activity in ethyl acetate rinses decreased exponentially with time, from the initial 90% to a low value of 27% 90 min after application. The corresponding values for AS-7N and AA-3409 were 93 and 46% and 97 and 64%, respectively, indicating that the adjuvants in the formulations exerted great influence on the penetration of the chemical. The increasing order of penetration observed in the present study is AID-585 > AS-7N > AA-3409. Beyond 90 min, the activity remaining on the cuticle leveled off, reaching nearly a constant value of 27% for AID-585, 46% for AS-7N, and 64% for AA-3409.

The increase and accumulation of radioactive aminocarb in the insect homogenates were exponential with time in all three formulations ( $^{14}\text{C}$ -activity in  $\text{CH}_3\text{CN}$  layer in Table 3). For AID-585, the activity increased rapidly from the initial 10% to 65% within 90 min after treatment and then reached a plateau. Similar trends were also observed for the other two formulations except that the 90-min peak levels were intermediate (51%) for AS-7N to low (33%) for AA-3409, confirming that cuticular penetration increased in the order of AID-585 > AS-6N > AA-3409 and that the oil carriers had exerted considerable influence on cuticular penetration compared to the emulsion formulation.

Insect cuticle is lipophilic due to the presence of lipids and hydrocarbons.<sup>4</sup> Lewis<sup>6</sup> reported that lipophilic solvents tend to spread rapidly over the surface of an insect under

TABLE 4  
Degradation of  $^{14}\text{C}$ -Aminocarb and Formation of Its Metabolites in Ethyl  
Acetate Rinses of Budworm

Time after application (min)	Percent of <sup>14</sup> C recovered from ethyl acetate rinses as indicated products*							
	A	MFA	MAA	FA	AA	DAP + MAP	Unknown	Total
Formulation: AA-3409								
0	97	0	0.5	0	0	0	0.5	98
15	93	0.5	1	0	0.5	0	1	96
30	91	0	2	0	1	0	3	97
45	90	0.5	2.5	0	1	0	3	97
60	86	1	4	0	2	0	4	97
90	80	1	3.5	0	3	0.5	7	95
120	77	0.5	2	0	2	0.5	9	91
150	73	0	2.5	0	1.5	0	12	89
180	70	0.5	1.5	0	2	0	16	90
Formulation: AID-585								
0	96	0	0	0	0	0	0	96
15	93	0	0.5	0	0.5	0	0	94
30	88	0	2	0	1	0	2	93
45	85	0.5	2	0	0.5	0	2	90
60	84	0.5	2.5	0	1	0	4	92
90	82	0	3	0	2	0	3	90
120	81	1	4	0	2	0	5	93
150	76	1	3	0	2	0	7	89
180	76	0	2	0	2	0	8	88
Formulation: AS-7N								
0	98	0	0	0	0	0	0	98
15	95	0	0.5	0	0	0	0	95.5
30	94	0	0.5	0	0.5	0	1	96
45	93	0	1	0	0.5	0	0.5	95
60	90	0.5	2	0	0.5	0	2	95
90	87	0.5	3	0	1.5	0	3	95
120	88	0	2	0	2	0	4	96
150	85	0.5	1.5	0	1	0	6	94
180	84	0	2	0	1	0	6	93

\* Values represent the mean for three replicate measurements. Standard deviations were less than 15% (not shown).

the influence of interfacial forces, facilitating penetration of solutes by intercalation in the wax layers, whereas aqueous solutions, being poor wetters of cuticle, do not penetrate cuticular layers rapidly. Aminocarb is moderately lipophilic ( $K_{ow} = 58 \pm 6$  at pH 7),<sup>10</sup> and if formulated in lipophilic solvents such as ID 585 and Sunspray® 7N (Table 2), it has a greater tendency to penetrate the hydrophobic insect cuticle and concentrate inside the body than when formulated as an emulsion.

Plots of the percent  $^{14}\text{C}$ -activity (Y) in ethyl acetate washes of insects (Table 3) vs. time (t) decreased curvilinearly and obeyed the exponential equation:

$$Y = A + Be^{-kt}$$



TABLE 5  
Degradation of  $^{14}\text{C}$ -Aminocarb and Formation of Its Metabolites in  
Acetonitrile Phase of Budworm Homogenate

Time after application (min)	Percent of <sup>14</sup> C recovered from acetonitrile phase as indicated products <sup>a</sup>							Total
	A	MFA	MAA	FA	AA	DAP + MAP	Unknown	
Formulation: AA-3409								
0	94	0	0.5	0	0	0	3.5	98
15	69	1	14	1	4	0	5	94
30	58	4	18	1	9	0	7	97
45	51	2	19	1	11	0	11	95
60	49	2	16	1	12	0	13	93
90	44	1	12	0	13	0	17	87
120	42	2	8	0.5	12	0.5	19	84
150	43	2	4	0	6	0	26	81
180	44	1	5	0.5	2	0.5	25	78
Formulation: AID-585								
0	96	0	0.5	0	0	0	1.5	98
15	75	0.5	9	0.5	3	0	4	92
30	64	2	15	1	5	0	6	93
45	60	1	16	0.5	7	0.5	9	94
60	53	1	14	1	9	0	11	89
90	50	0.5	7	0.5	10	0	15	83
120	51	1	5	0.5	7	0.5	17	82
150	49	0	6	0	6	0	18	79
180	52	0.5	3	0.5	3	0	20	79
Formulation: AS-7N								
0	96	0.5	0.5	0	0	0	1	98
15	82	1	8	0	2	0	3	96
30	76	1	11	1	4	0	6	99
45	70	0.5	13	0.5	7	0	7	98
60	67	1	13	0	8	0	7	96
90	63	0.5	10	0.5	6	0	12	92
120	64	1	7	0	4	0	13	89
150	63	0.5	4	0.5	4	0	15	87
180	64	0.5	5	0.5	4	0	16	85

\* Values represent the mean for three replicate measurements. Standard deviations were less than 15% (not shown).

where A represents the percent residual  $^{14}\text{C}$ -activity remaining in ethyl acetate over time, B represents the percent activity penetrated, and K is the rate constant. Nonlinear regression analysis of the data (ethyl acetate rinses in Table 3) gave the values for A, B, K, and  $R^2$  (coefficient of determination) for the three formulations and are recorded in Table 6. The value A (residual activity in ethyl acetate) for AID-585 is lower (23.0%) and increases to 43.0% for AS-7N and then to 59.2% for AA-3409, indicating that cuticular penetration is relatively high for AID-585 and decreases in the order AID-585 > AS-7N > AA-3409. Correspondingly, the value of B (penetrated activity) is high for AID-585 (66.9%) and gradually decreases to 49.8% for AS-7N, and further to 37.9% for AA-3409, confirming that better insecticide diffusion has occurred in aminocarb formulations containing the oil



TABLE 6  
Penetration Characteristics of Formulated Aminocarb in Spruce Budworm  
Following Topical Application and Regression Coefficients A, B, and C of the  
Exponential Equation  $Y = A + Be^{-Kt}$  for Ethyl Acetate Rinse

Formulation abbreviation	A (% residual activity on insect surface)	B (% residual activity penetrated in insect)	K (penetration rate constant)	$T_{1/2}$ (min) for 50% penetration	$R^2$ (%) (coefficient of determination)
AA-3409	59.2	37.9	-0.018	—	0.96
AID-585	23.0	66.9	-0.029	31.40	0.99
AS-7N	43.0	49.8	-0.025	78.17	0.98

carriers compared to emulsion. Between the two oil formulations, the values of A and B clearly demonstrate that the low-viscosity carrier oil ID-585 promoted the diffusion of aminocarb more through the insect cuticle compared to the high-viscosity Sunspray® 7N. The rate constant K, representing the rapidity of  $^{14}\text{C}$ -activity penetrated, increases (becomes more negative) from -0.018 for AA-3409 to -0.029 for AID-585, confirming the role of lipophilic adjuvants in cuticular penetration. The half-life ( $T_{1/2}$ ) is lower for AID-585 (31.40 min) than for AS-7N (78.17 min), confirming that low-viscosity oil adjuvants such as ID-585 are very effective in promoting penetration of the a.i. compared to the high-viscosity adjuvants such as Sunspray® 7N. The value of A (residual activity on the insect surface) for AA-3409 is 59.2% (Table 6); therefore, no  $T_{1/2}$  value could be calculated for this formulation.

The average bound residues for AID-585, AS-7N, and AA-3409 were about 0.3, 0.2, and 0.5%, respectively, with a noticeable increase in value for AA-3409 from 0.2 to 0.8% with time. With oil formulations, such a definite increase was not apparent (Table 3). The average total recovery ranged from 100.2 to 88.7% for AID-585, 100.2 to 95.7% for AS-7N, and 100.8 to 94.3% for AA-3409. Considering the uncertainties and errors involved in the experimentation, the recoveries reported in Table 3 are considered as quantitative.

#### B. INFLUENCE OF PHYSICAL PROPERTIES ON CUTICULAR PENETRATION

The measured physical properties (density, viscosity, and surface tension) of the three formulations are given in Table 2. Except for viscosity, the other two properties of the formulations are nearly the same. Consequently, their contributions to surface migration and the spreading of the droplet on the insect cuticle would be the same for all three formulations. Surface migration and spreading of droplets are a function of surface tension and viscosity.<sup>6</sup> Solutions of low viscosity can spread quickly over insect cuticle under the influence of interfacial forces, facilitating penetration of active ingredients.<sup>3,6</sup> In addition to lipophilicity, the low viscosity of AID-585 contributed to the rapid penetration of the insecticide solute through the cuticle. Contrary to this, the poor penetration of the active material in AA-3409, although its viscosity is the lowest, is attributable to its poor wettability of the hydrophobic cuticle and meager solubility of the solute particulates (2 to 3  $\mu\text{m}$  in size) in the emulsion media. The viscosity of the AS-7N formulation is the highest in the series, but the toxicant has penetrated through the cuticle to an appreciable extent (Table 3). Evidently, factors other than viscosity are involved. Sunspray® 7N is nonvolatile and functions as a carrier for aminocarb particulates. Since it is lipophilic, we can hypothesize that the solvent will diffuse, spread, and migrate into the lipids of the epicuticle, thereby disorganizing the wax layer and facilitating the transport of the solute by diffusion across the epicuticle. The rate of

intoxication for a contact toxin is directly related to the rate of its penetration through the exposed insect cuticle.<sup>6</sup> Therefore, the choice of adjuvant in formulating commercial spray mixes, their solvent properties, and a thorough understanding of their interacting processes that take place at the epicuticle are important to obtain maximum efficiency in spray operations.

### C. METABOLIC FATE OF AMINOCARB

The aminocarb, its metabolites containing intact carbamate moieties (MFA, MAA, FA, and AA), and the two phenolic mixtures (DAP + MAP) found in the ethyl acetate rinses and acetonitrile layers over the study period are given in Tables 4 and 5, respectively. Excluding the unknowns, the major components were the parent material and the mono (MAA)- and di (AA)-N-demethylated products. The metabolites detected were similar to those found in other studies.<sup>1,11,21</sup> Low levels of MFA were found frequently in the rinses and homogenates, whereas FA was found in small amounts in the acetonitrile layer only (Table 5). The phenolic moieties (DAP + MAP) were found occasionally at very low levels (activity 0.5%) in both liquid phases. Although the amount of products found in the rinses and homogenates varied, the pattern and spectrum of products formed in both were similar. In order of decreasing concentration, the major metabolites in both liquid phases (Tables 4 and 5) were MAA, AA, MFA, and FA (FA was found frequently at low levels in the acetonitrile phase), with sporadic presence of the phenols (DAP + MAP).

The percent activity of aminocarb in the ethyl acetate layer (Table 4) decreased from 97 to 70 for AA-3409, from 96 to 76 for AID-585, and from 98 to 84 for AS-7N. Correspondingly, a gradual increase in the activities of MAA and AA were observed in all cases, reaching maximum values around 90 min, and thereafter, their activities decreased. Contrary to these, the activities of the unknowns gradually increased with time as chemical and enzymatic degradations continued. The activity levels of the metabolites, and the unknowns formed, varied according to the formulation type.

The percent <sup>14</sup>C-activity of aminocarb recovered from the acetonitrile phase (Table 5) decreased with time, from 94 to 44 for AA-3409, from 96 to 52 for AID-585, and from 96 to 64 for AS-7N. The decrease is probably due to the increased metabolic activity with time. Apart from four- to fivefold increases in the quantities of the identifiable metabolites (Table 1) and two- to threefold increases in the unknowns, the pattern of degradation of aminocarb and the formation of metabolites (increase in MAA and AA initially with time followed by their decrease, and increase of unknowns with time) in the homogenates were similar to those found in the cuticular rinses.

The occasional formation of small amounts (0.5%) of the phenolic moieties (DAP + MAP) in the rinses and homogenates indicate that hydrolysis of the carbamate ester bond is not a predominant reaction in this study, contrary to the observations made elsewhere.<sup>12</sup> Nothing is known about the identity of the unknown metabolites detected on the TLC plate, including the ones at the origin. We may speculate that some of them may be products formed by ring hydroxylation and deamination, and by oxidation of ring-amino (H<sub>2</sub>N-Ar), ring-methyl, or carbamate methyl groups through the oxidative microsomal enzymes in the insect. The transformation products at the origin appear to be more polar, and they may be amino acid or glucosidic conjugate moieties containing phenolic, carboxylic, and amino groups. The formation of such conjugates has not been demonstrated in budworm, but such a possibility cannot be ruled out.

Attempts to obtain the mass balance for the data recorded in Tables 4 and 5, with the assumption that the activities of the ethyl acetate rinses and acetonitrile extracts (Table 3) are 100% each, were successful only for the surface wash wherein >88% of the assumed value was recovered. However noticeable deviations (only >78% recovery) occurred for

the extract, especially beyond 90 min. No possible explanation could be given for this discrepancy.

From the results presented in Tables 4 and 5 and from the foregoing discussions, the major degradative pathway of aminocarb in eastern spruce budworm appears to be successive oxidative N-demethylation of the dimethylamino group, first forming MFA, followed by the formation of the corresponding transient carboxylic acid and decarboxylation of the acid to yield MAA. Similar degradative steps of MAA would yield first FA and then AA. Hydrolysis of A and MAA would yield the corresponding phenols DAP and MAP. In the case of MAP, it is not known whether the hydrolysis of MAA preceded oxidation or vice versa. Apart from the parent material, the stable and most prominent degradation products in the study are MAA and AA. The sequence of transformation steps outlined above for aminocarb in the insect is somewhat speculative, but the pattern of products formed is in agreement with the fate of closely related compound, mexacarbate (which differs from aminocarb only in possessing a methyl group in ring position 5), in western spruce budworm.<sup>14</sup>

### ACKNOWLEDGMENTS

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## Chapter 12

**THE CHARACTERIZATION OF UPTAKE AND TRANSPORT  
WITH A RADIOLABELED ARYLOXYPHENOXYPROPIONATE  
HERBICIDE AS INFLUENCED BY ADJUVANTS****Robert L. Noveroske, F. Nelson Keeney, and J. Graham Brown****TABLE OF CONTENTS**

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## ABSTRACT

In order to study the impact of various adjuvants on the uptake and translocation of aryloxyphenoxypropionate herbicides, high pressure liquid chromatography (HPLC) studies were conducted to compare the metabolic profiles from treated and untreated plant fractions of giant foxtail (*Setaria faberi* Herrm.) treated with a foliar application of  $^{14}\text{C}$ -haloxyfop {2-[4-[[3-chloro-*s*-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propionic acid}. Similar metabolic profiles were found to exist between the treated leaf tissue and the export fraction.

Experiments were then conducted with various adjuvants being added to the standard formulation. Crop oil concentrate (COC) and crop oil (CO) were more effective in increasing uptake and transport than nonionic wetters. The combination of CO plus wetter resulted in the most efficient level of  $^{14}\text{C}$ -uptake and -transport. Subsequent bioassay studies confirmed the benefit of CO-nonionic wetter blends in maximizing herbicidal activity.

The resultant enhanced biological response of the active ingredient permitted the design of formulations containing sufficient volumes of CO and wetter in the formulation concentrate itself, which on dilution with water in the spray tank did not require additional adjuvant. Use of radiotracer techniques are a highly effective means by which to quantitatively select adjuvants, wetters, and their combinations in order to define formulations with maximum performance potential.

## I. INTRODUCTION

The biological activity of a postemergence systemic herbicide is dependent upon its physical and chemical properties, and interactive processes on and in the plant. The availability of the active ingredient at the active site is a function of its ability to penetrate the plant cuticle and the translocation and metabolic processes within the plant. The interaction of processes occurring on the plant surface — volatilization, degradation, and penetration — and the resultant impact on active ingredient available for transport have been studied in detail.<sup>10</sup>

Esters of haloxyfop, such as haloxyfop-methyl and haloxyfop-ethoxyethyl, have been developed for postemergence grass control with excellent selectivity to soybeans and other broadleaf crops.<sup>1,15,16</sup> As with other aryloxyphenoxypropionates, the esters penetrate readily, followed by rapid hydrolysis to the acid,<sup>5,7,10</sup> the active ingredient in the plant.<sup>3,13,14</sup> Further metabolic activity may result in formation of conjugates within the plant which may act as a hydrolyzable source of active ingredient.<sup>8,14</sup>

Considerable effort has been spent studying the effect of adjuvants on increasing the activity of postemergence herbicides.<sup>2-4,6,11,12,15</sup> Among the variety of adjuvants tested, petroleum oils applied as tank-mix additives have been found to provide the most consistent levels of improved activity with aryloxyphenoxypropionates.<sup>4,6,10</sup> Tank-mix combinations of COC (1.25% v/v) and nonionic wetter (0.25% v/v) were found to be the most effective treatment for enhancing the activity of {3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carboxyl]amino]sulfonyl]-2-thiophencarboxylic acid}, a sulfonylurea herbicide, on *Kochia* sp. under stressed plant conditions.<sup>12</sup>

Uptake and transport studies with radiolabeled haloxyfop-methyl were initiated in an attempt to understand the influence of adjuvants on enhancing the mobilization of  $^{14}\text{C}$ -activity into the plant, in order to optimize formulation design and behavior. This chapter summarizes the results of the impact of various adjuvant blends on formulation performance as measured by the uptake and transport of the  $^{14}\text{C}$ -labeled active ingredient after foliar applications of radiolabeled haloxyfop-methyl on giant foxtail.



TABLE I  
Adjuvant Compositions and Manufacturers

Adjuvant	Manufacturer	Composition
Multifilm X-90	IWD, Ltd.	Polyoxyethylene (9) nonyl phenyl ether
Polyglycol 59-13	Dow Chemical U.S.A.	Polyoxyethylene (8) tridecyl ether
Atplus 411F crop oil concentrate (COC)	ICI Americas, Inc.	83-85% Paraffin oil and 15-17% non-ionic emulsifier
Sunspray 11E crop oil (CO)	Sun Oil Co.	97% Paraffin oil and 3.0% nonionic emulsifier

The ultimate goal of this research was to gain sufficient insight on uptake phenomena so as to be able to design delivery systems which contained active ingredient and adjuvants in concentrations sufficient to provide the performance level and handling characteristics desired without having to resort to additional tank-mixing efforts.

## II. MATERIALS AND METHODS

### A. ADJUVANT STUDIES

A series of petroleum-based adjuvants and nonionic wetters were evaluated in the greenhouse to determine their potential to enhance the activity of haloxyfop-methyl and haloxyfop-ethoxyethyl for control of quackgrass (*Elytrigia repens* (L.) Nevski) and foxtails (*Setaria* spp.). A list of adjuvants, their composition, and corresponding manufacturer are shown in Table 1.

Seeds were planted in drainable, polyethylene pots (5 × 5 × 8 cm) containing Jiffy mix. Established seedlings were thinned to 0.1 to 0.2 plants per cm<sup>2</sup>. All pots were watered with one-half strength Hoagland's solution as needed. the greenhouse was maintained at 25 ± 5°C with a light intensity of 550 μE m<sup>-2</sup> s<sup>-1</sup> photosynthetically active radiation. Supplemental lighting maintained a photoperiod of 15 h.

Plants were grown to the three- to four-leaf stage (requiring approximately 14 d) before herbicide treatment. Plants were selected for uniformity and treated with foliar applications of formulated haloxyfop-methyl and haloxyfop-ethoxyethyl as emulsifiable concentrates (ECs). All treatments were applied in a spray chamber with an automated track sprayer operating at 4.8 km/h and 46 cm above the plant canopy with a T-Jet flat fan nozzle calibrated to deliver a total spray volume of 187 l/ha at 276 kPa. The soil surface was covered with vermiculite absorbent prior to treatment to prevent soil activity of the individual herbicides. It was removed after the spray treatments were dried.

Treatment replications were randomized and plants were watered with one-half strength Hoagland's solution by subirrigation as needed. Plants were graded for growth reduction relative to controls which included formulation inerts, using a scale of 0 to 100% (0 = no effect, 100 = total kill). GR<sub>80</sub> values were calculated using linear regression analysis. The GR<sub>80</sub> values reported reflect the amount of active ingredient needed, expressed as grams of acid equivalent (a.e.) per hectare, to provide 80% control.

### B. RADIOTRACER STUDIES

Three- to four-leaf-stage seedlings (10 to 11 d old) of giant foxtail were used for all <sup>14</sup>C-studies. Plants were grown in a vermiculite-Jiffy mix blend (50:50) in drainable polyethylene pots (5 × 5 × 8 cm deep) under the same nutritional schedule, temperature, and light conditions as described for greenhouse bioassays. Experiments were conducted in an environmental chamber with a light intensity of 220 μE m<sup>-2</sup> s<sup>-1</sup> and a temperature of 28°C. Plants were incubated in the chamber for 24 h before being treated.

The radiolabeled formulation was prepared by adding  $^{14}\text{C}$ -haloxyfop-methyl-ph-UL- $^{14}\text{C}$  with a specific activity of 19.98 mCi/mmol to the EC formulation blank. Treatments were prepared in crimp-top micro vials by adding the formulation to tap water (pH 8.2 to 8.4). Optionally, wetter and CO were added as dictated by the experiments.

Applications were made to the second, fully expanded leaf from the apex with a micro-syringe at the rate of 140 g a.e./ha in 187 l of total spray volume. Additional replicates of leaf tissue were treated and immediately rinsed for 10 s in 5 ml of acetonitrile (ACN) in scintillation vials to determine zero-time application concentrations. Ten milliliters of Aquasol were added and the samples counted in a liquid scintillation counter (LSC). The ACN-rinsed leaves were combusted in a tissue oxidizer and the amount of  $^{14}\text{CO}_2$  generated was determined using LSC techniques. Rinses and combustions were used collectively to establish the dose applied.

At desired time intervals in each experiment, four replications of each treatment were harvested. Treated leaves were removed, rinsed in ACN for 10 s to remove unabsorbed  $^{14}\text{C}$ -activity, and counted using LSC techniques to establish the amount of  $^{14}\text{C}$ -activity which had not penetrated the plant. The rinsed leaves were combusted in a tissue oxidizer and assayed for  $^{14}\text{CO}_2$  using LSC techniques to establish the amounts of  $^{14}\text{C}$ -activity associated with the treated leaf which had penetrated (leaf uptake minus transport). Plants were cut at the soil line, roots carefully removed from the potting medium, and combusted to reflect  $^{14}\text{C}$ -basipetal transport. In a like manner,  $^{14}\text{C}$ -activity associated with the untreated above-ground portion of the plant (untreated leaves) was determined. Leaf uptake plus transport values were used collectively to quantify uptake, the total fraction which had penetrated into the plant. Recoveries of  $^{14}\text{C}$ -activity were expressed as a percent of the total amount applied to plants at zero time.

### C. HPLC STUDIES

HPLC analyses were conducted using a Waters HPLC equipped with a 30.0-cm micro Bondapak  $\text{C}_{18}$  column. Twenty-four hours after treatment, leaves were removed and rinsed sequentially with ACN to remove surface residues. Treated and untreated plant portions were homogenized and extracted in 50% ACN, and 200- $\mu\text{l}$  aliquots of these extracts were chromatographed and assayed by HPLC. The solvent system employed as 0 to 100% ACN with 1.0% acetic acid over 20 min, then held for 10 min. The flow rate was 1.5 ml/min, with eluent collected in 1.0-min fractions. HPLC chromatograms of  $^{14}\text{C}$ -haloxyfop-methyl and haloxyfop were developed in this solvent system for reference purposes.

## III. RESULTS AND DISCUSSION

Experiments were conducted on *Setaria* spp. to correlate biological activity with  $^{14}\text{C}$ -uptake and transport patterns, and to study adjuvant effects resulting from postemergence applications of radiolabeled haloxyfop-methyl. Results of a greenhouse bioassay comparing the effectiveness of a standard EC formulation (XRM-4570), alone and tank mixed with COC (1.25% v/v), with that of a high emulsifier-containing formulation (XRM-4685) are summarized in Table 2.

Tank-mix applications of COC substantially improved the activity of XRM-4570. XRM-4685 containing high (50% w/w) emulsifier provided a measurable improvement in activity when compared with XRM-4570. Wetter concentrations from the formulations at their respective  $\text{GR}_{80}$  levels differed about fourfold. Adjuvant benefits from nonionic wetters are generally detectable at concentrations of 0.05% (v/v) and higher.<sup>9</sup> The results of this experiment are consistent with this observation. An experiment was conducted on *S. faberi* with radiolabeled haloxyfop-methyl as XRM-4570 and XRM-4685, both with and without

TABLE 2  
Effect of Adjuvants on the Activity of Haloxyfop-  
Methyl for Control of *Setaria lutescens*\*

Treatment	Adjuvant conc % (v/v/187 l/ha)	GR <sub>50</sub> (g a.e./ha)
XRM-4570 <sup>a</sup>	0.016	89.79
XRM-4570 + 1.25% COC	1.250	33.64
XRM-4685 <sup>b</sup>	0.063	56.22

\* Dow Chemical U.S.A., 1985.

<sup>a</sup> 240 g a.e./l EC.

<sup>b</sup> 240 g a.e./l EC — high emulsifier content.

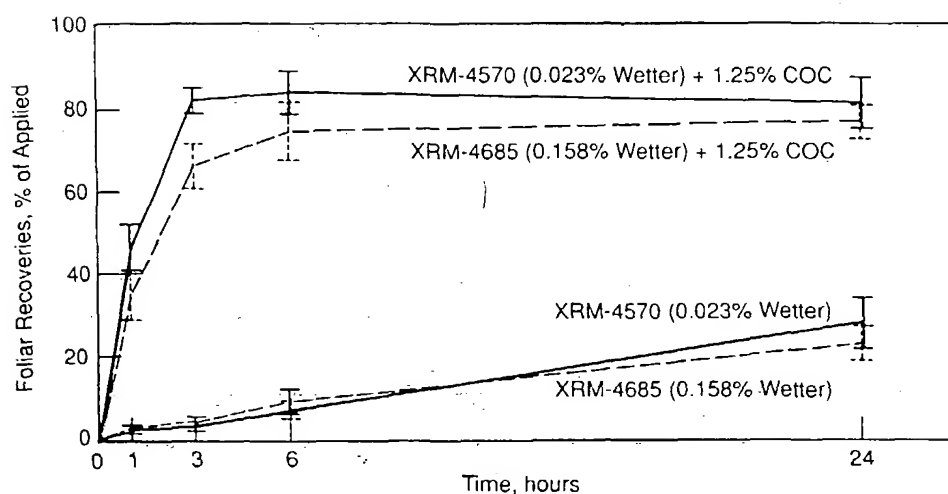


FIGURE 1. The effect of adjuvants on uptake of  $^{14}\text{C}$ -activity from leaves of *S. faberi* treated with haloxyfop-methyl (140 g ae/ha).

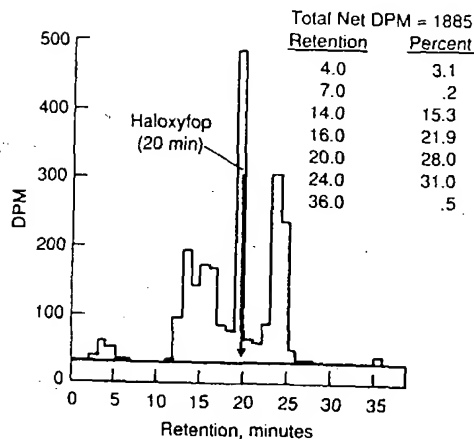
tank mixes of COC (1.25%, v/v), to determine the impact of formulation and adjuvants on  $^{14}\text{C}$ -uptake. The results are summarized in Figure 1.

Applications of COC markedly enhanced foliar uptake of  $^{14}\text{C}$ -activity from both formulations. Differences due to wetter concentration between the two formulations were not detected, as was the case in the bioassay (Table 2). Lack of agreement is not believed due to species differences, since earlier work had shown no differences in  $^{14}\text{C}$ -uptake patterns between the two formulations with and without COC when tested on *S. faberi* and *S. lutescens*.<sup>9</sup>

A possible explanation may be the impact of the increased deposition on the leaf surface when the composition was applied with a track sprayer, compared with radiotracer applications which utilized a microsyringe to apply a few droplets to the plant leaf. Alternatively, uptake may not be the rate-limiting process which can be used to judge formulation behavior in bioassays.

An experiment was conducted to determine the metabolic profiles of  $^{14}\text{C}$ -activity from treated vs. untreated portions, so as to establish a relationship between the nature of the  $^{14}\text{C}$ -residues in treated vs. transported plant fractions. HPLC chromatograms from extracts

## HPLC HISTOGRAM I

XRM-4570 24-Hr Uptake *S. faberi*

## HPLC HISTOGRAM II

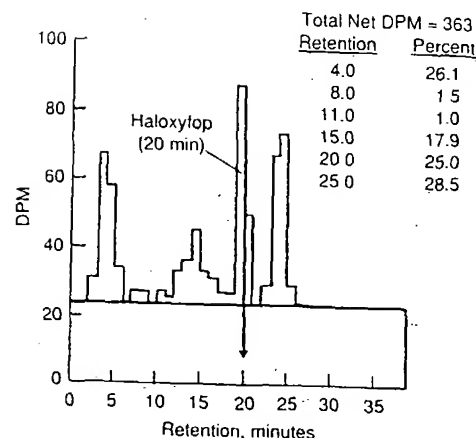
XRM 4570 24-Hr Export *S. faberi*

FIGURE 2. HPLC profiles of radioactivity from extracts of treated (I) and untreated (II) plant tissue of *S. faberi* 24 h after a foliar application of haloxypop-methyl as XRM-4570 at 140 g a.e./ha in 187 l of water.

of treated and untreated plant tissue of *S. faberi* were developed 24 h after a foliar application of  $^{14}\text{C}$ -haloxypop-methyl as XRM-4570 at 140 g a.e./ha in 187 l of water (Figure 2).

Peaks with a retention time identical to that of haloxypop (20 min), the active ingredient in the plant,<sup>3,13,14</sup> were found in approximately similar concentrations in the extracts, along with several metabolites proposed to be conjugates.<sup>10</sup> No parent ester was detected, consistent with the findings that aryloxyphenoxypionate esters are rapidly hydrolyzed by the plant.<sup>5,7,10</sup>

From these results, it was concluded that a similar metabolic profile exists between treated leaf tissue and export fractions and that, depending upon the experimental objectives and sensitivity needed, total  $^{14}\text{C}$ -activity from either fraction could be useful in quantifying the benefits of adjuvants in studying formulation behavior.

An experimental 120 g a.e./l of EC formulation of haloxypop-methyl containing 25 wt% each of nonionic emulsifier and CO was prepared which was found to exhibit acceptable handling properties. A radiolabeled sample was prepared and  $^{14}\text{C}$ -transport compared with  $^{14}\text{C}$ -haloxypop-methyl as XRM-4570, with and without a tank mix of COC (Figure 3).

Levels of  $^{14}\text{C}$ -transport with the experimental formulation were similar to those realized by XRM-4570 plus 1.25% COC, despite the fact that CO-wetter concentrations at finished dilutions were appreciably lower (0.07% each, 0.14% total) than contained in the XRM-4570 + COC treatment (0.012% wetter + 1.25% COC). This suggests that ratios of wetter and oil may exist which may improve the performance of an active ingredient, allowing the use of appreciably lower levels of oil than conventionally used in tank-mix practices.

A greenhouse bioassay was conducted in which a dilution series of haloxypop-ethoxyethyl was bioassayed with a dilution series of CO as Sunspray® 11E and the wetter Polyglycol 59-13, each alone and in combination (Table 3).

At the high (50 g a.e./ha) rate, good adjuvant benefits resulted from each of CO and wetter independently, when compared to the no-adjuvant treatment. At the median (25 g a.e./ha) rate, control of *Elytrigia repens* was markedly enhanced by combinations of CO and wetter. Concentrations of 12.5 g a.e./ha were too low to detect any adjuvant benefits.

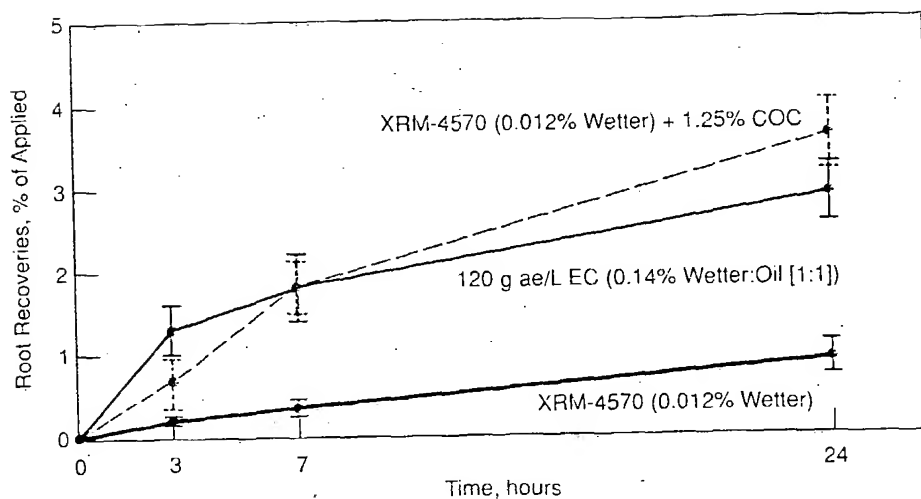


FIGURE 3. The effect of adjuvants on basipetal transport of  $^{14}\text{C}$ -activity from leaves of *S. faberi* treated with haloxyfop-methyl (70 g ae/ha).

TABLE 3  
Effect of Adjuvants on the Activity of Haloxyfop-Ethoxyethyl  
for Control of *Agropyron repens*\*

Treatment	Adjuvant Conc. % (v/v)/300 l/ha	% control 22 DAT, g a.e./ha			
		0.0	12.5	25.0	50.0
EF-646* + No Adjuvant			0.0	0.0	0.0
Sunspray 11E	0.125		5.0	0.0	100.0
	0.500		0.0	5.0	100.0
	1.000		0.0	25.0	100.0
	0.010		0.0	0.0	30.0
PG 59-13	0.050		0.0	25.0	100.0
	0.100		0.0	40.0	100.0
	0.125 ± 0.010		0.0	65.0	100.0
Sunspray 11E + PG 59-13	0.500 + 0.010		0.0	65.0	100.0
	0.125 ± 0.050		0.0	100.0	100.0
	0.500 ± 0.050		30.0	95.0	100.0
Untreated		0.0			

\* Dow Chemical Europe, King's Lynn, 1984.

\* 104 g a.e./l EC.

A field experiment was conducted comparing the adjuvant effects of oil, wetter, and oil-wetter combinations on haloxyfop-ethoxyethyl for control of large crabgrass [*Digitaria sanguinalis* (L.) Scop.] (Table 4). The results of this experiment support the  $^{14}\text{C}$ -transport conclusions (Figure 3), confirming the benefit of CO-wetter adjuvant combinations and their effectiveness in maximizing activity.

Based upon the above experimental results, it is concluded that the use of radiotracer techniques are of value in quantifying the effects of adjuvants on the uptake and transport



TABLE 4  
Effect of Adjuvants on the Activity of Haloxyfop-Ethoxyethyl for  
Control of *Digitaria sanguinalis*\*

Treatment	Adjuvant Conc, % (v/v)/200 l/ha	% brownout (150 g a.e./ha) trial	
		I — 70 DAT	II — 56 DAT
XRM-4638 <sup>a</sup> +			
Sunspray 11E	1.000	90.0	85.0
Multifilm X-90	0.300	65.0	73.0
Sunspray 11E + Multifilm X-90	0.150 + 0.150	85.0	90.0
	0.200 + 0.100	72.0	80.0
	0.225 + 0.075	85.0	85.0
CV		10.0	10.0

\* Dow Chemical Pacific, New Zealand, 1986.

<sup>a</sup> 240 g a.e./l EC.

of <sup>14</sup>C-activity in plants from postemergence application of radiolabeled herbicides. When used in conjunction with bioassays, such techniques represent a powerful research tool by which to characterize the performance of an active ingredient, study formulation behavior, and optimize delivery systems.

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## ACTIVATION OF THE FOLIAR UPTAKE OF TWO WATER-SOLUBLE COMPOUNDS BY ALCOHOL POLYOXYETHYLENE SURFACTANTS

David Stock, Peter J. Holloway, Paul Whitehouse, and B. Terrence Grayson

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## ABSTRACT

The influence of four  $C_{13}/C_{14}$  fatty alcohol surfactants with mean ethylene oxide contents of 6, 11, 15, and 20 on the foliar uptake of  $^{14}C$ -labeled solutions of methylglucose and phenylurea by field (broad) bean (*Vicia faba* L.) and wheat (*Triticum aestivum* L.) was investigated under controlled environment conditions. Surfactant concentration and ethylene oxide content were found to influence greatly the uptake of the two compounds. Uptake activation only occurred when a threshold concentration of surfactant was exceeded. Uptake of  $^{14}C$ -methylglucose was greatest in the presence of surfactants of high ethylene oxide content, while that of  $^{14}C$ -phenylurea was much less sensitive to surfactant structure. Marked differences in the amount of movement of radiolabel were observed between field bean and wheat following applications of  $^{14}C$ -phenylurea formulations, but these could not be ascribed to the properties of the surfactants added.

## I. INTRODUCTION

Surfactants are used routinely as spray adjuvants to enhance the field performance of pesticide formulations. However, while the uptake and performance-promoting properties of nonionic surfactants have been exploited in commercial pesticide formulation, remarkably little is known about how this activation is achieved. Some research, however, has provided circumstantial evidence for specific mechanisms of activation, such as copenetration of surfactant with the active ingredient<sup>9,13</sup> and a humectant action of the surfactant.<sup>12,13</sup>

It is our view that a better understanding of structure-activity relationships is needed as a basis for detailed studies of the mechanisms of surfactant-induced activation of foliar uptake. There is very little information in the open literature dealing systematically with effects of either surfactant structure or concentration on the foliar uptake of agrichemicals; many reports describe the influence of a random selection of nonionic, cationic, and anionic compounds with little attention being paid to concentration. Some more extensive surveys have been conducted, however, into the enhancement effects of nonionic surfactants on the activity of a number of herbicides.<sup>5,10,15</sup>

Factorially designed radiochemical uptake studies have already demonstrated the importance of the physicochemical properties of the penetrating molecule in influencing the optimal surfactant structure needed for its activation.<sup>4</sup> The object of this chapter is to illustrate the importance of both surfactant structure and concentration in enhancing the uptake of foliage-applied compounds. It describes work on the uptake-promoting properties of a series of fatty alcohol polyoxyethylene surfactants when added to formulations of two model water-soluble compounds. Parallel work at Long Ashton Research Station (LARS) with similar, radiolabeled surfactants is directed at establishing the exact mechanism(s) involved in foliar uptake activation by this class of nonionic surfactant.

## II. MATERIALS AND METHODS

### A. PLANT MATERIAL

Two plant species were used for uptake studies. Field bean (cv. Maris bead), which has leaves with little epicuticular wax, was selected to contrast with wheat (cv. Minarette), which has a microcrystalline, water-repellent deposit of foliar wax.

All plants were raised from seed and grown in 9-cm pots of Arthur Bower's peat-based compost. After initial propagation in a greenhouse, plants were transferred to a controlled environment (CE) room at least 2 weeks before experimentation. Field bean plants were

used for uptake experiments 3 weeks after sowing, and wheat plants after 4 weeks. The CE room provided a 20°C (light)/15°C (dark) temperature regime with a 16-h photoperiod of 300  $\mu\text{mol m}^{-2} \text{s}^{-1}$  provided by fluorescent tubes supplemented with tungsten lamps. The humidity of the CE room was not regulated, but followed a regular diurnal pattern of 71 to 81% relative humidity (RH) during the light period and 88 to 93% RH in the dark.

#### B. ALCOHOL POLYOXYETHYLENE SURFACTANTS

This surfactant class is frequently used in pesticide formulations. Four members of the Marlupal 34 series (Hüls, Marl, Germany), with mean molar ethylene oxide (E) contents of 6, 11, 15, and 20, and hydrophile-lipophile balance (HLB) values of 11.2, 14, 15, and 16.2, respectively, were selected. The parent primary alcohol (A) for the series is a  $\text{C}_{13}/\text{C}_{14}$  mixture, with straight-chain compounds accounting for 45% of the total. The remainder consists of methyl branched homologues.

#### C. WATER-SOLUBLE MODEL COMPOUNDS

Two radiolabeled compounds were investigated: 3-*O*-methyl- $\alpha$ -D-glucose and phenylurea.

Methylglucose is a highly water-soluble monosaccharide with an estimated log P (octanol/water partition coefficient) of  $\sim 3.0$ . The 3-*O*-methyl-D-[U- $^{14}\text{C}$ ]glucose (50  $\mu\text{Ci}/\text{mmol}$ ) was obtained from Amersham.

Phenylurea (log P 0.8) is structurally related to a number of herbicides and is much less water soluble (4086 ppm) than methylglucose.  $^{14}\text{C}$ -carboxyl-labeled phenylurea was synthesized at LARS and had a specific activity of 11.5  $\mu\text{Ci}/\text{mg}$ .

#### D. EXPERIMENTAL DESIGN

A  $4 \times 3$  factorial design was used, with the four selected surfactants at concentrations of 0.02, 0.1, and 0.5% (w/v). Test compounds were added to each formulation at a fixed concentration of 0.05% (w/v); a control treatment without any added surfactant was also included. Four replicates were used per treatment at each sampling interval.

#### E. PREPARATION AND APPLICATION OF TREATMENT SOLUTIONS

Treatment solutions (100  $\mu\text{l}$ ) were prepared in angle-bottomed vials<sup>2</sup> 1 h before each experiment. All treatment solutions contained about 5000 dpm/ $\mu\text{l}$  and were formulated in acetone-water (1:1) to ensure comparability with other investigations at LARS involving compounds of low water solubility.<sup>4</sup> Other workers<sup>11</sup> have established that the presence of a volatile organic solvent does not significantly influence the foliar uptake process.

Droplets were applied to leaves using a Burkard PAX-100 Programmable Microapplicator fitted with a 50- $\mu\text{l}$  syringe.<sup>2</sup> Applications were performed inside the CE room, as were subsequent samplings. Treatment solutions were applied as  $10 \times 0.2$ - $\mu\text{l}$  droplets to the central region of the adaxial surface of the third leaf of field bean plants and to the same region of the youngest fully expanded leaf of wheat plants.

#### F. DETERMINATION OF UPTAKE

Uptake was determined at various time intervals after application of radiolabeled formulations. Suitable sampling intervals were selected from the results obtained from preliminary experiments using AE15 at 0.1% (w/v).

Two methods were used to determine the uptake of  $^{14}\text{C}$  into the plant. Radioactive surface deposits were removed by cellulose acetate stripping from the treated area of the leaf.<sup>7</sup> This method removes any superficial deposits together with the crystalline epicuticular

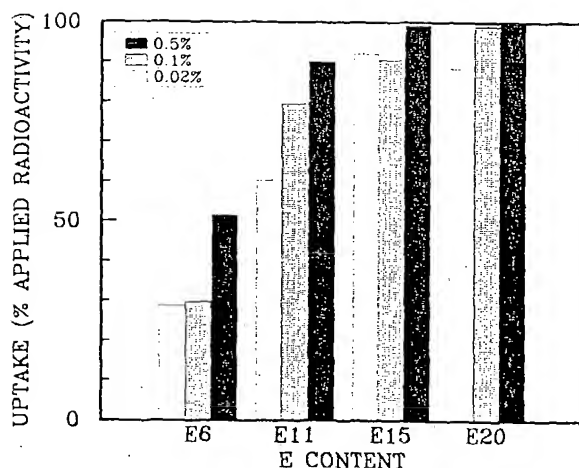


FIGURE 1. Influence of concentration and E content of a  $C_{17}/C_{18}$  alcohol series of surfactants on uptake of radiolabel from a 0.05% (w/v) solution of  $^{14}\text{C}$ -methylglucose 1 d after droplet application to wheat leaves. In the absence of added surfactant, there was about 10% uptake of radiolabel. Values plotted are the means of four replicates; the standard error of the difference of the means for the 12 treatments is 4.5.

wax layer. Radioactivity was determined by liquid scintillation counter (LSC) analysis after the cellulose acetate strip was dissolved in a dioxan-based cocktail.

Combustion-LSC analysis of the excised treated area, after removal of the surface deposit, was used to determine the amount of radioactivity in the treated leaves. Tissue was oxidized in a stream of oxygen at  $900^{\circ}\text{C}$  and the  $^{14}\text{CO}_2$  generated was trapped in an amine-based cocktail for subsequent LSC analysis. If the total amounts of radioactivity recovered from the surface deposit and within the treated area were substantially less than that originally applied, the proximal (basipetal movement) and distal portions (acropetal movement) of the treated leaf were combusted to quantify any movement of radioactivity.

### III. RESULTS AND DISCUSSION

#### A. INFLUENCE OF SURFACTANT CONCENTRATION ON FOLIAR UPTAKE

There was a strong influence of surfactant concentration on the foliar uptake of the two test compounds (Figures 1 through 4), the highest surfactant concentration invariably promoting the greatest enhancement of uptake irrespective of surfactant structure. This is well illustrated by the uptake of radiolabel from  $^{14}\text{C}$ -phenylurea on field bean after 1 d (Figure 4), where the uptake was about 20% in the presence of 0.02% (w/v) surfactant while it was about 95% at 0.5%. The highest surfactant concentration used often caused phytotoxic damage at the site of original droplet application; similar damage has been noted by workers with other surfactants.<sup>5,6,8,14</sup> However, in our experiments, the occurrence of such symptoms did not appear to impede foliar absorption.

The uptake data obtained also indicated that a threshold concentration of surfactant is probably necessary before significant activation of the uptake of any compound can occur. For example, for the uptake of  $^{14}\text{C}$ -methylglucose into CE-grown wheat (Figure 1), the activation threshold of AE15 and AE20 is 0.02% or lower. However, a concentration in excess of 0.1% is required to activate a similar amount of uptake of phenylurea into the same species (Figure 2). The factors which govern these different threshold levels are not fully understood, but are likely to be the nature of the penetrating compound, the nature of



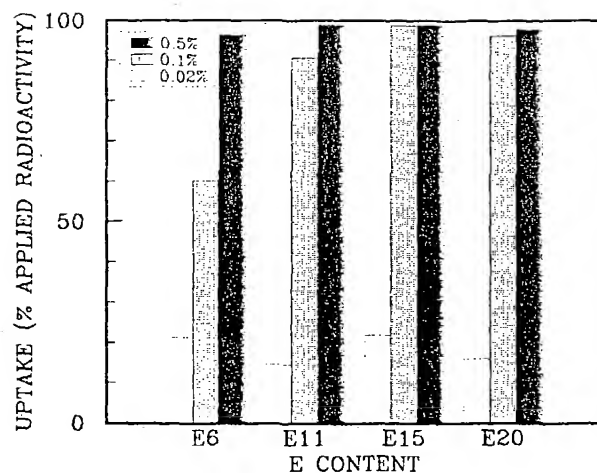


FIGURE 2. Influence of concentration and E content of a  $\text{C}_{13}/\text{C}_{14}$  alcohol series of surfactants on uptake of radiolabel from a 0.05% (w/v) solution of  $^{14}\text{C}$ -phenylurea 1 d after droplet application to wheat leaves. In the absence of added surfactants, there was about 6% uptake of radiolabel. Values plotted are the means of four replicates; the standard error of the difference of the means for the 12 treatments is 4.3.

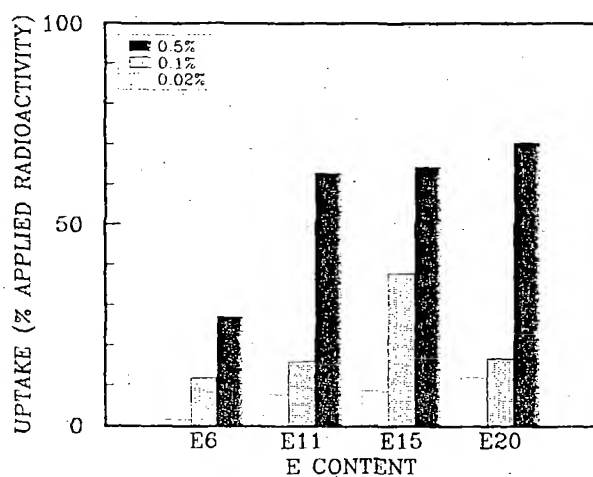


FIGURE 3. Influence of concentration and E content of a  $\text{C}_{13}/\text{C}_{14}$  alcohol series of surfactants on uptake of radiolabel from a 0.05% (w/v) solution of  $^{14}\text{C}$ -methylglucose 1 d after droplet application to field bean leaves. In the absence of added surfactant, there was about 8% uptake of radiolabel. Values plotted are the means of four replicates; the standard error of the difference of the means for the 12 treatments is 5.2.

the surfactant, and the plant species treated.<sup>4</sup> It is planned to use radiolabeled surfactants added to formulations to investigate this phenomenon.

#### B. INFLUENCE OF SURFACTANT STRUCTURE ON FOLIAR UPTAKE

Surfactant structure had a significant influence on the foliar uptake of  $^{14}\text{C}$ -methylglucose and  $^{14}\text{C}$ -phenylurea on both plant species after 1 d (Figures 1 through 4). Similar effects have been observed for alkylphenol surfactants on the biological activity of three water-



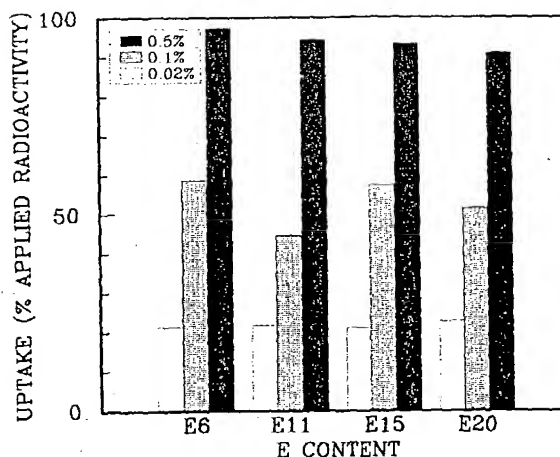


FIGURE 4. Influence of concentration and E content of a  $C_{13}/C_{14}$  alcohol series of surfactants on uptake of radiolabel from a 0.05% (w/v) solution of  $^{14}C$ -phenylurea 1 d after droplet application to field bean leaves. In the absence of added surfactant, there was about 13% uptake of radiolabel. Values plotted are the means of four replicates; the standard error of the difference of the means for the 12 treatments is 5.2.

soluble herbicides on maize,<sup>1,10</sup> where there was an optimum E range of 15 to 20; higher and lower E members of the surfactant series were less effective activators. Such investigations, however, involved spray application with the complicating factors of retention and redistribution of the active ingredients. These factors are not present in the uptake work reported here.

Uptake activation of the highly water-soluble methylglucose is especially sensitive to E content, AE20 promoting the greatest uptake activation after 1 d (on wheat, 99.6% uptake of radiolabel in the presence of AE20 at 0.5%). Uptake of a related compound, 2-deoxyglucose, has been positively correlated with the hygroscopicity of octylphenoxy surfactants,<sup>12</sup> which increases with E content.<sup>13</sup> A moisture-retaining humectant action of AE surfactants, increasing with E content, is therefore a possible explanation for the activation results observed for methylglucose. This hypothesis could be confirmed by using  $^{14}C$ -surfactants: it would be predicted that humectants will not penetrate, or penetrate at very low rates relative to that of the test compound, if they are to maintain the surface deposit of a soluble test compound in a hydrated state suitable for foliar uptake.

A relationship between the optimum foliar uptake of a compound, its log P, and the E content of alcohol polyoxyethylene surfactants has recently been proposed by us.<sup>4</sup> Using a response surface model, we postulate that there would be a shift in E content for optimal uptake-promoting properties from high E-content AE surfactants for low log P compounds to low E-content members for high log P compounds. However, in the central region of the model surface, the structural requirements in terms of E content for uptake promotion of compounds of intermediate log P are less distinct. Phenylurea is thought to be close to this so-called critical log P region, which is likely to vary according to plant species, thus explaining the relative lack of surfactant structural effects on the uptake of phenylurea, especially on field bean (Figure 4). A slight, but statistically significant, structural preference for higher E-content surfactants for uptake activation of phenylurea is, however, observed on wheat (Figure 2).

The findings reported here emphasize the need to select the correct surfactant structure and concentration for optimal activation of the foliar uptake of a particular compound.

**TABLE 1**  
**Uptake and Movement of Radiolabel in Field Bean 1 Day after Foliar**  
**Application of  $^{14}\text{C}$ -Phenylurea Solutions (0.05%, w/v) Containing AE6 and**  
**AE15, Each at Three Different Concentrations**

Surfactant	Concentration (%, w/v)	Surface* deposit	Region within treated leaf <sup>b</sup>		Recovery
			Treated area	Distal	
AE6	0.02	79 (5)	10 (1)	4 (1)	93
	0.1	41 (12)	47 (9)	13 (6)	101
	0.5	3 (1)	67 (10)	30 (10)	100
AE15	0.02	79 (10)	13 (4)	4 (1)	96
	0.1	43 (13)	44 (9)	15 (5)	102
	0.5	7 (2)	73 (3)	24 (3)	104

*Note:* Values expressed as a percentage of the radioactive dose applied; standard deviations of the mean of four replicates are given in parentheses.

\* Determined by cellulose acetate film stripping.

<sup>b</sup> Determined by combustion analysis of cellulose acetate stripped leaves.

However, increasing the concentration of a less efficient activator surfactant may compensate for its lack of structural suitability. This is well illustrated by comparing the activating effects of AE6 at 0.5% and AE11 at 0.02% on the uptake of  $^{14}\text{C}$ -methylglucose on wheat after 1 d (Figure 1). In this situation, a 25-fold greater concentration of AE6 is required to promote a magnitude of uptake activation similar to that of AE11 at 0.02%, i.e., 50% uptake of radiolabel compared to 60% for AE11.

Our findings also show that different uptake activation profiles for the same compound may be obtained, depending on the plant species treated. A good example is the uptake of  $^{14}\text{C}$ -methylglucose on field bean (Figure 3) and on wheat (Figure 1), where a lower surfactant threshold is observed for wheat (0.02%), as is a more distinct gradient in the efficiency of uptake activation from AE6, which is least effective, to AE20, which promotes the greatest activation relative to the control treatment on both species. Superimposing data plotted in the form of response surfaces should reveal the maximum selective difference in the uptake of a compound between a target and nontarget species. This may not necessarily occur with the surfactant-concentration combination which produces the most efficient uptake activation on the target plant, such as a weed species. As Jansen et al.<sup>5</sup> have pointed out, judicious selection of surfactants could, therefore, lead to more effective targeting of pesticides.

### C. INFLUENCE OF SURFACTANTS ON MOVEMENT OF RADIOACTIVITY

No movement of radiolabel out of the treated area was recorded for any formulations of  $^{14}\text{C}$ -methylglucose applied to field bean leaves. Proximal and distal leaf portions were, accordingly, not retained for the subsequent experiment using  $^{14}\text{C}$ -methylglucose on wheat. However, significant loss of radiolabel (about 20% of the applied dose) was observed following uptake of the same formulations by wheat. Subsequent experiments have revealed that this is due to a combination of acropetal transport and metabolism.

Proximal and distal portions of treated leaves were analyzed for AE6 and AE15 treatments in combination with  $^{14}\text{C}$ -phenylurea on both wheat and bean plants. However, only acropetal transport of radiolabel was observed in both species. In field bean (Table 1), there would appear to be a general relationship between the amount of uptake and the quantity of radiolabel moving into the distal leaf portion 1 d after application. The amount of radiolabel in the

TABLE 2  
Uptake and Movement of Radiolabel in Wheat 1 Day after Foliar  
Application of  $^{14}\text{C}$ -Phenylurea Solutions (0.05%, w/v) Containing AE6  
and AE15, Each at Three Different Concentrations

Surfactant	Concentration (%, w/v)	Surface deposit <sup>a</sup>	Region within treated leaf <sup>b</sup>		Recovery
			Treated area	Distal	
AE6	0.02	79 (6)	3 (1)	13 (1)	95
	0.1	40 (8)	8 (3)	49 (6)	97
	0.5	4 (1)	3 (1)	90 (2)	97
AE15	0.02	78 (8)	3 (1)	16 (3)	97
	0.1	1 (1)	4 (1)	91 (4)	96
	0.5	1 (1)	5 (2)	95 (4)	101

<sup>a</sup> Determined by cellulose acetate film stripping.

<sup>b</sup> Determined by combustion analysis of cellulose acetate stripped leaves.

distal leaf portion is about 25% of that recovered from within the treated leaf. Thus, there is no specific effect of surfactant structure or concentration on the movement of radiolabel. Results obtained from applications of  $^{14}\text{C}$ -phenylurea to wheat illustrate a different pattern of movement of radioactivity (Table 2). Between 3 and 8% of penetrated radiolabel is retained within the treated area, while the bulk of the radioactivity is translocated into the distal leaf portion. Rapid movement in the acropetal direction therefore occurs following penetration. As with field bean, no specific relationship exists between movement of radiolabel and surfactant characteristics. The phytotoxic damage to the application site observed for AE15 at 0.5% had little influence on the transport of radioactivity in the treated leaves after 1 d.

It would thus seem probable that transport phenomena which occur after cuticular penetration of an agrichemical are not greatly influenced by surfactants — a suggestion first put forward by Foy and Smith.<sup>1</sup> However, in some situations, cellular damage may impair the movement of systemic compounds. Transport is determined, therefore, primarily by an interaction between the plant species and the test compound, while AE surfactants exert their influence almost exclusively at the penetration stage. Movement of nonionic surfactants away from the site of uptake is usually limited,<sup>1,3,9</sup> suggesting that their interaction with mobile active ingredients subsequent to uptake is minimal.

#### IV. CONCLUSION

The work conducted at LARS and elsewhere has shown that many problems remain unresolved in the field of foliar uptake, especially the exact mechanisms of uptake activation and the way in which such mechanisms may vary between different classes of surfactant. It is only from systematic uptake investigations of the type reported here, coupled with similar research on retention and distribution phenomena, that rational guidelines for optimal surfactant selection will be established. This should allow a predictive element in formulation development, ultimately reducing the amount of empirical work involved in the optimization of formulations. In addition, a better understanding of the mechanisms involved may lead to new uses for existing environmentally safe pesticides.

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**EFFECT OF POLYSORBATE SURFACTANTS WITH VARIOUS  
HYDROPHILIC-LIPOPILIC BALANCE (HLB) VALUES ON  
LEAF SURFACE ULTRASTRUCTURE AND MOBILITY OF  
METHAZOLE IN PLANTS AND SOIL**

Chester L. Foy and Tsuneyuki Takeno

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## ABSTRACT

Polysorbate surfactant (hydrophile-lipophile balance [HLB] 4.3) eroded cotton (*Gossypium hirsutum* L.) leaf surfaces severely at 1% (w/w) concentration, as shown by scanning electron photomicrography. Reticulated and etched patterns were observed on cotton leaf surfaces treated with water-soluble surfactants. Trichomes on the leaves of prickly sida (*Sida spinosa* L.) did not appear to be affected by the surfactants. Leaves of prickly sida were less affected than those of cotton. The surface deposits of formulated methazole were different in appearance from those of technical methazole. The  $^{14}\text{C}$ -methazole and/or its  $^{14}\text{C}$ -labeled metabolites moved acropetally in the treated leaves of cotton and prickly sida. This pattern was not altered with polysorbate surfactants with different HLB values. Total uptake and distribution of  $^{14}\text{C}$  increased with increasing concentration of methazole and decreasing HLB values of surfactants. More  $^{14}\text{C}$  was translocated in cotton than in prickly sida. The effects of surfactants were masked by the drastic solvent action of 100% methanol. When the solvent effect was subtracted, the surfactant with HLB 8 caused the greatest enhancement of translocation in both species. Radiolabeled methazole leached poorly in a silt loam soil and was either slightly retarded or unaffected by added surfactants. The influence of HLB of polysorbate surfactants on  $^{14}\text{C}$ -methazole mobility was minimal.

## I. INTRODUCTION

Herbicides have been used to control weeds, one of the major economic problems in agriculture, for many years, and during this period many new herbicides with diverse chemical properties have been developed. Herbicides and plant growth regulators sprayed onto plant surfaces commonly encounter plant epidermal waxes as the first barrier to penetration. Multiple forms of wax excretions from leaves, shoots, and fruits were described by Amelunxen et al.<sup>1</sup> Measurement of the contact angle of a droplet applied to foliage is one method of determining the wettability of the plant surface by the solution. Hall et al.<sup>9</sup> combined contact angle determinations with scanning electron microscopy and found that contact angles in excess of  $145^\circ$  occurred on leaves when numerous wax rods or plates covered their surfaces. Silva Fernandes<sup>24</sup> studied the water repellency of surface waxes with electron microscopy and classified the surface waxes as water repellent and non-water repellent. A crystalline or semicrystalline wax repelled water and a noncrystalline wax did not repel water.

Wortman<sup>31</sup> used electron microscopy to study the changes in the surfaces of leaves caused by pesticides and a wetting agent. Ong et al.<sup>23</sup> observed leaf surfaces upon which herbicide was sprayed by using a scanning electron microscope (SEM) equipped to detect fluorescence and reported a new, rapid method for spatially localizing herbicides on leaf surfaces. Hess et al., using similar techniques, conducted a series of experiments on herbicidal dispersal patterns as a function of leaf surface,<sup>10</sup> mapping residues using X-ray fluorescence,<sup>11</sup> and as a function of formulation.<sup>12</sup>

Polysorbate surfactants, nonionic polyoxyethylated derivatives of sorbitan fatty acid esters, have been used as additives to herbicidal formulations and are sometimes found to effectively enhance their herbicidal activity. The properties of nonionic surfactants are known to be changed with the hydrophilic-lipophilic-balance (HLB).

The optimum surfactant HLB requirement will change from system to system. Umoessien et al.<sup>29</sup> reported that the absorption and general phytotoxicity of linuron [*N'*-(3,4-dichlorophenyl)-*N*-methoxy-*N*-methylurea] and prometryn [*N,N'*-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine] were enhanced by surfactants within the HLB range of 5.4 to 15.0. Morton and Combs<sup>21</sup> found the greatest herbicidal enhancement of a picloram (4-



amino-3,5,6-trichloro-2-pyridinecarboxylic acid)-2,4,5-T [(2,4,5-trichlorophenoxy)acetic acid] mixture with surfactants within the HLB range of 13.3 to 15.4. Hull and Shellhorn<sup>14</sup> treated seedlings of mesquite (*Prosopis juliflora* (Sw.) DC) with the butoxyethyl ester of 2,4,5-T in various combinations of phytotoxic and nontoxic oils and nonionic surfactants of HLB 8.6 and 1.8, and found that when sorbitan monolaurate (HLB 8.6) was used with phytotoxic oils, subsequent apical epinasty and repression of growth was greater than with other combinations. Ethoxylated stearyl ether and amine surfactants at HLB 15 to 16 and 19 to 20, respectively, gave optimum effectiveness of glyphosate [N-(phosphonomethyl)glycine] against common milkweed (*Asclepias syriaca* L.) and hemp dogbane (*Apocynum cannabinum* L.); surfactants with a low HLB value were usually less effective.<sup>32</sup> Penetration of 2,4-D[(2,4-dichlorophenoxy)acetic acid] and NAA (2-naphthaleneacetic acid) in apple (*Malus pumila* M.) increased linearly as various surfactant HLBs decreased from 14.6 to 3.5.<sup>27</sup>

Tween 20 (HLB 16.7) showed a contact angle of 85.5 to 98.0% on intact leaf surfaces on four rice cultivars; these were the smallest in a Tween series having HLB values in the range of 11.0 to 16.7.<sup>20</sup> The surface tension of polyoxyethylene (POE) nonylphenyl ethers, POE octylphenyl ethers, POE sorbitans, and polystearylphenols was lowest in the range of 12 to 14 HLB.<sup>8</sup> The contact angle on the leaf surface of rice (*Oryza sativa* L.) increased with an increase in HLB value, showing the lowest in the range of 10 to 13 HLB.

Chemical additives applied to plant or soil before, with, or after herbicide treatment reach the soil and, conceivably, may modify adsorption, absorption, mobility, leaching, diffusion, accumulation, and metabolism of the herbicide in such a way as to alter its activity and residual fate. Numerous studies involving the effects of adjuvants on plant surfaces<sup>15</sup> and in plants<sup>22</sup> have been conducted; however, relatively little information is available concerning the modifying effects of adjuvants on the distribution, availability, and persistence of herbicides in soil.<sup>3</sup>

Methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione] is a selective herbicide for use in cotton (*Gossypium hirsutum* L.) and shows good selectivity in several other crops.<sup>30</sup> Methazole controls selected broadleaf weed species, including prickly sida (*Sida spinosa* L.). The extent and scientific bases of herbicidal selectivity between cotton and prickly sida have been reported.<sup>6,7,16,17</sup>

Bond and Roberts<sup>4</sup> reported little movement of methazole in soil in field studies. In leaching-column experiments, both methazole and its metabolites were relatively immobile.<sup>5,26</sup> The results of studies by Koskinen<sup>19</sup> indicated that methazole is highly adsorbed by soil organic matter, does not readily desorb, and can degrade rapidly.

The experiments described herein were conducted to evaluate the possible influence of polysorbate surfactants having different HLB values on (1) the plant cuticular structure and how polysorbate surfactants were deposited on the leaf surface, (2) absorption and translocation of <sup>14</sup>C-methazole in cotton and prickly sida plants (absorption and translocation of <sup>14</sup>C-labeled polysorbate surfactants were evaluated also), and (3) the depth of leaching of <sup>14</sup>C-methazole in soil.

## II. MATERIALS AND METHODS

### A. LEAF SURFACE STUDIES

Span 80® (nonionic surfactant containing sorbitan monooleate, HLB 4.3), Tween 80® (nonionic surfactant containing polyoxyethylene sorbitan monooleate, HLB 15.0), and their mixtures of 65/35 (w/w) Span 80/Tween 80 (HLB 8.0) and 28/72 (w/w) Span 80/Tween 80 (HLB 12.0) were used in this investigation. Surfactant solutions were prepared by first dissolving the surfactants in 5 g of absolute ethanol and then diluting to 100 g with distilled water. Also, an ethanol-aqueous solution (5%, w/w) and absolute ethanol were included to evaluate the solvent effect.

Methazole (99.4%, w/w) active solution was prepared by dissolving 0.8 g in 99.2 g of ethanol. Methazole in a 75% wettable powder form was prepared by adding 98.9 g of distilled water to 1.1 g of powder.

Cotton ("Deltapine") and prickly sida seedlings 8 to 10 and 18 to 20 d old, respectively, were placed in jars containing one-half strength Hoagland and Arnon's<sup>13</sup> nutrient solution No. 1 supplemented with 5 ppm Sequestrene 138 Fe [sodium ferric ethylenediamine di-(*o*-hydroxyphenyl acetate)]. The plants were grown under greenhouse conditions until the cotton and prickly sida plants were 30 and 45 d old, respectively. At the time of treatment, the cotton plants were 18 to 22 cm in height with two primary leaves fully expanded; prickly sida plants were 15 to 20 cm in height at the seven- to eight-leaf stage of growth.

The primary leaf of cotton and the fourth leaf of prickly sida were dipped for 1 min in 100 ml of 0.1 or 1.0% (w/w) polysorbate surfactant solution, or solvent, solvent-aqueous, or methazole spray solution. The treated leaves were cut at the petiole 3 and 72 h after treatment and two discs of approximately 6 mm in diameter were cut from each species. The leaf discs, one for study of the adaxial surface and another for observation of the abaxial surface, were fixed on metal holders with silver enamel and placed in a vacuum chamber. A uniform coating of palladium-gold was evaporated onto the surface. The samples were fully prepared within the day of harvest and observed by use of a high-resolution AMR Model 900 SEM.

## B. MOBILITY STUDIES IN PLANTS

Stock solutions of Span 80 (HLB 4.3) and Tween 80 (HLB 15.0) were prepared by dissolving 200 mg of each in methanol and distilled water, respectively. Solutions with HLBs of 8 and 12.0 were prepared by mixing the stock solutions of the two surfactants at the same ratios described earlier.

The <sup>14</sup>C-methazole used was heterocyclic ring-labeled in the number 3 carbon (specific activity, 7.6 mCi/mmol). A stock solution was prepared by dissolving 100  $\mu$ Ci of <sup>14</sup>C-methazole in 10 ml of methanol. Various treatment solutions were made by dilution of the stock solution with surfactant solution, methanol, or distilled water.

In studies using radiolabeled surfactants, stock solutions of <sup>14</sup>C-Span 80 labeled in the fatty acid moiety (1  $\mu$ Ci/mg) and <sup>14</sup>C-Tween 80 labeled in the fatty acid moiety (0.25  $\mu$ Ci/mg) were prepared by dissolving 100 mg each in 10 ml of methanol and distilled water, respectively. Radiolabeled surfactant solutions with HLBs of 8.0 and 12.0 were prepared in the same manner as were nonlabeled surfactant solutions. Because of the different specific activities of Span 80 and Tween 80, the amount of radioactivity applied for each HLB value varied; therefore, count data were corrected for 0.1- $\mu$ Ci applications.

Cotton and prickly sida plants were grown and treated at the same ages and growth stages described earlier. A 20- or 25- $\mu$ l drop containing <sup>14</sup>C-methazole (0.1  $\mu$ Ci) in methanol or 1% (w/v) surfactant solutions having different HLB values and methanol content was applied to the midrib of one primary leaf of cotton and the fourth leaf of prickly sida. In the treatments for studying foliar absorption of labeled surfactants, approximately 0.1  $\mu$ Ci of labeled surfactant in methanol or methanol-aqueous solution was applied in the same way. The treatment was localized by confining the solution in lanolin rings. Duplicate plants were harvested 3, 24, and 72 h after treatment. At the end of the treatment periods, the lanolin paste was removed and the treated spot was removed with a cork borer. The plants were sectioned into roots, stems, and leaves and processed for autoradiography. Following autoradiography, treated lamina and their petioles were ground, suspended in Aquasol Universal L.S.C. Cocktail, and counted using a 3000 Series Packard Tri-Carb liquid scintillation counter.

### C. MOBILITY STUDIES IN SOIL

A stock solution was prepared by dissolving 100  $\mu\text{Ci}$  of  $^{14}\text{C}$ -methazole in 10 ml of acetone. Various treatment solutions were made by diluting the stock solution with nonradiolabeled methazole, surfactant, and acetone. The same surfactants — Span 80, Tween 80, and their mixtures — employed in earlier experiments were used.

Plastic straws 6 mm in diameter and 21 cm long were used as soil columns. The bottom of each column was packed with a small amount of glass wool. The columns were uniformly filled with 4.5 g of a silt loam soil (1.4% organic matter) which had been oven dried at 70°C for 10 d and sieved to pass through a 40-mesh screen.

Methazole at 0.22 g/m<sup>2</sup> and surfactants at these concentrations were applied in a 20- $\mu\text{l}$  acetone solution to the surface of the soil so that there was 0.25, 1.0, and 4.0 times as much surfactant present on a weight basis. Each 20- $\mu\text{l}$  treatment solution contained 1.9  $\mu\text{g}$  (0.1  $\mu\text{Ci}$ ) of  $^{14}\text{C}$ -methazole and 3.1  $\mu\text{g}$  of nonradiolabeled methazole.

After the soil had dried from the herbicide treatment, the columns were leached with 10 ml of distilled water, which was added continuously to maintain a water level at least 5 mm deep on the soil surface. The soil columns were kept at the same position for 4 h after irrigation and then placed at the horizontal position in a 70°C oven for 24 h. The columns were then sectioned in 1-cm lengths from the top of the soil and oven dried an additional 48 h. The straw shells were removed and the soil was suspended in a liquid scintillation cocktail and counted as described earlier.

## III. RESULTS AND DISCUSSION

### A. LEAF SURFACE STUDIES

SEM micrographs of natural leaf surfaces of cotton, which did not receive any treatment, are shown in Figures 1A and 1B. The cuticle in the cotton covered the epidermal cells smoothly, and it was difficult to locate the boundary between cells as reported by Troughton and Donaldson.<sup>28</sup> The stomata appeared to be somewhat more numerous on the abaxial than on the adaxial side of the leaves (Figures 1A through 1F). Both surfaces of the cotton treated with 100% ethanol were dehydrated and exhibited complex fibrous wax structures (Figures 1C and 1D). A louver-like structure of leaf waxes was observed outside the guard cells on the adaxial surface. These results suggest that the ethanol solubilized and removed some of the waxes from the leaf surfaces, so that they were dehydrated and shrunken. Figures 1E and 1F illustrate the results of the treatment of cotton with 5% (w/w) ethanol-aqueous solution, which was used as a solvent for polysorbate surfactants. The epidermal cells were shrunken and the surfaces wrinkled. The stomata of the abaxial surface were open wider than those of the adaxial surface (Figures 1E and 1F).

Leaf surfaces of cotton treated with 1% (w/w) surfactant, HLB 4.3) solutions were more drastically affected than those treated with other surfactant solutions (Figures 2A through 2H). The surfactant accumulated in the troughs of irregular corrugations of the leaf surface 3 h after treatment (Figure 2A), and then severely eroded the leaf wax structure 72 h after treatment (Figure 2B). The stomatal openings were masked with Span 80 and/or eroded leaf waxes (Figure 2B). Accumulation of the surfactant in the troughs of irregular corrugations was also observed with 0.1% (w/w) surfactant (HLB 4.3), but severe erosion of the surface waxes was not observed (micrographs not shown). Erosion and etching of leaf surfaces were not observed with 1% (w/w) surfactant with HLB 8.0 (Figures 2C and 2D). Cotton leaves treated with 1% (w/w) surfactant (HLB 12.0) had a network of cracked cuticle which covered the epidermal cells 3 h after treatment (Figure 2E). The stomata of the leaf 72 h after treatment with the same solution had not closed at that stage, but other epidermal cells shrank and the surface became wrinkled (Figure 2F). Cotton leaves treated with 1.0% (w/

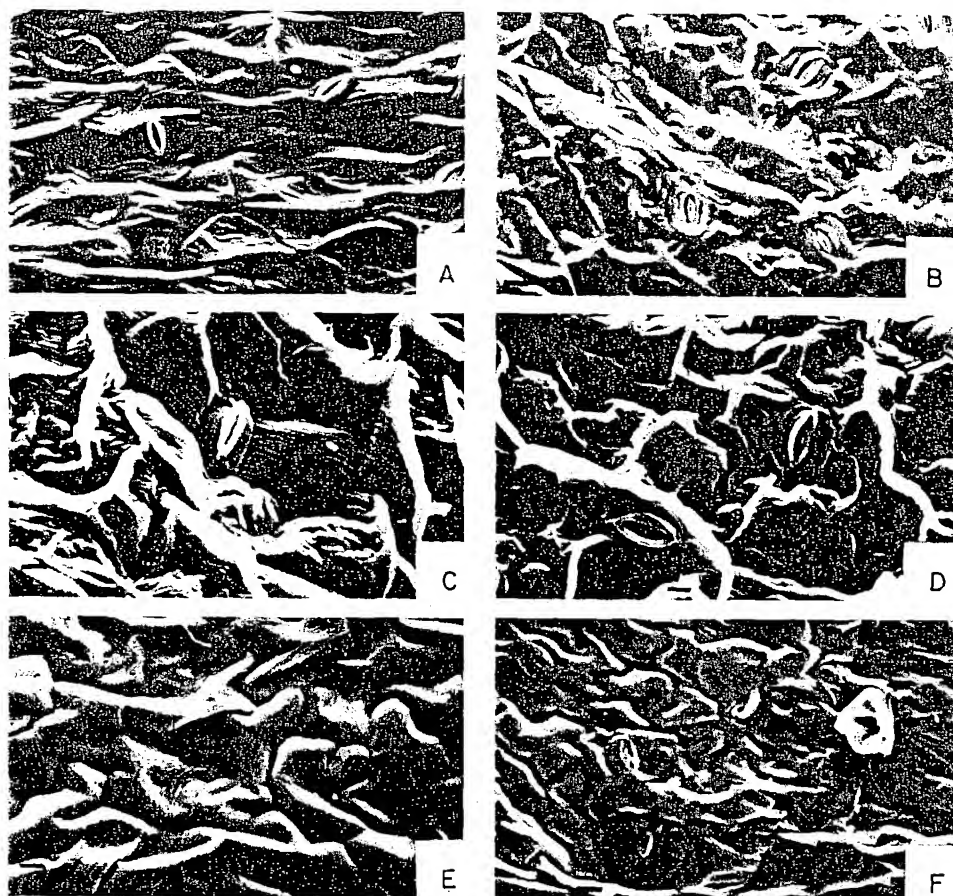


FIGURE 1. SEM micrographs of cotton leaf surfaces. (A) Adaxial surface of untreated leaf; (B) abaxial surface of the same leaf; (C) adaxial surface of leaf 3 h after dipping in 100% ethanol; (D) abaxial surface of the same leaf; (E) adaxial surface of leaf 3 h after dipping in 5% (w/w) ethanol-aqueous solution; (F) abaxial surface of the same leaf. Scale represents 10  $\mu$ .

w) surfactant (HLB 15.0) had cracked surfaces (Figure 2G and 2H) which resembled leaf surfaces treated with polysorbate surfactant with HLB 12.0. The pattern may have been water-soluble surfactants themselves, which spread over the leaf, dried, and then cracked because of low affinity for leaf waxes.

The leaf surfaces of prickly sida which did not receive any treatment are shown in Figures 3A and 3B. The leaf surfaces of prickly sida appear smooth to the naked eye, but numerous trichomes were observed on both sides of the leaf by SEM. These trichomes have a narrow, needle-like upper part and some of them have branched, multicellular, stellate hairs (Figures 3B and 3D). Prickly sida leaves dipped in 100% ethanol were severely dehydrated (Figures 3C and 3D). Leaf surfaces treated with 5% (w/w) ethanol solution were similar to those of untreated leaf, suggesting that the 5% ethanol solution did not significantly influence the cuticle of the prickly sida leaf (Figures 3E and 3F).

About 3 h after treatment with surfactant (HLB 4.3) solution, numerous small brown spots appeared on both sides of the leaf of prickly sida; they then turned black within 72 h. SEM micrographs taken over those discolored regions of the leaf show that Span 80 was



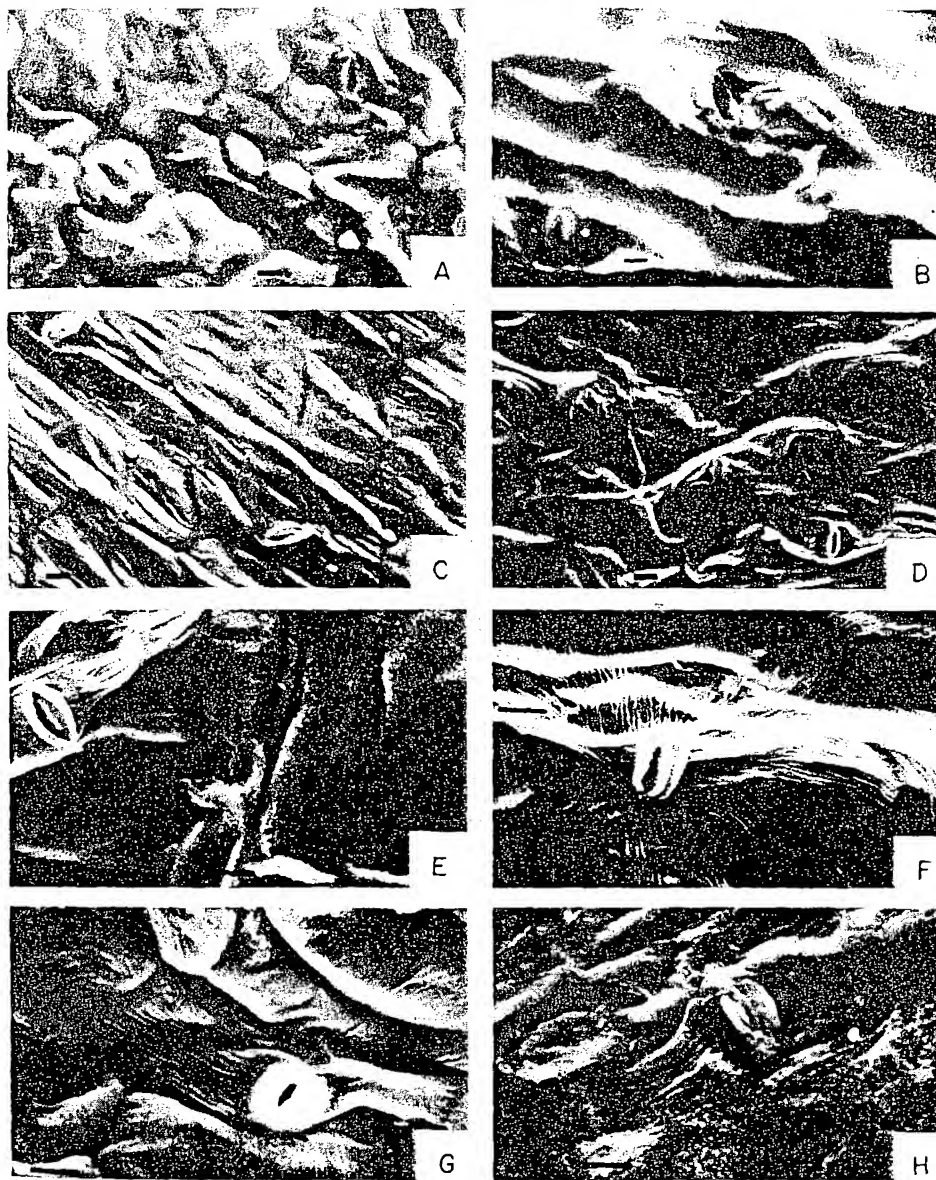


FIGURE 2. SEM micrographs of adaxial surfaces of cotton after dipping in 1% (w/w) surfactant solutions. HLB 4.3 at 3 h (A) and 72 h (B) after dipping; HLB 8.0 at 3 h (C) and 72 h (D) after dipping; HLB 12.0 at 3 h (E) and 72 h (F) after dipping; HLB 15.0 at 3 h (G) and 72 h (H) after dipping. Scale represents 10  $\mu$ .

deposited on the leaf surfaces like oil drops (Figures 4A and 4B). Prickly sida leaves treated with surfactant (HLB 8.0) solutions were more dehydrated than those treated with preparations with other HLB values (Figures 3A, 3B, and 3E through 3H). Figures 4E through 4F are SEM micrographs of prickly sida treated with water-soluble surfactant (HLB 12.0 and 15.0) solutions. No remarkable changes in leaf cuticle were observed. Trichomes were apparently not affected by these surfactants.

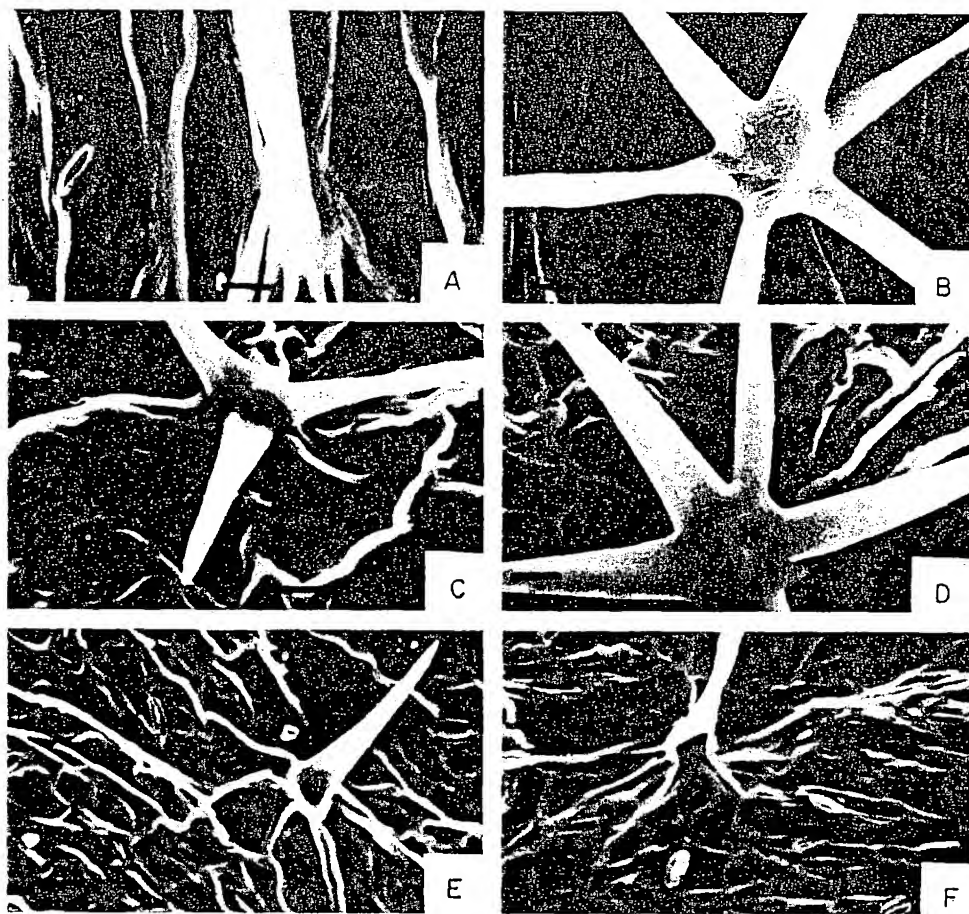


FIGURE 3. SEM micrographs of prickly sida leaf surfaces. (A) Adaxial surface of untreated leaf; (B) abaxial surface of the same leaf; (C) adaxial surface of leaf 3 h after dipping in 100% ethanol; (D) abaxial surface of the same leaf; (E) adaxial surface of leaf 3 h after dipping in 5% (w/w) ethanol-aqueous solution; (F) abaxial surface of the same leaf. Scale represents 10  $\mu$ .

Crystallized methazole was observed on the leaf surfaces of both plant species treated with 0.8% (w/w) technical methazole ethanol solution (Figures 5A and 5C). Wettable powder suspensions of methazole caused deposits on the leaf surfaces of both plant species that were readily observed (Figures 5B and 5D). The amounts of chemicals deposited on the leaves of prickly sida were greater than on the leaves of cotton.

#### B. MOBILITY STUDIES IN PLANTS

Autoradiograms of the 72-h foliar treatment of cotton and prickly sida indicated that methazole remained in the treated leaf and moved apoplastically, regardless of the surfactant HLB and methanol content (Figure 6). The distribution of  $^{14}\text{C}$  in the veins and closely associated tissues of both cotton and prickly sida increased with the concentration of methanol in the treatment solutions, and also increased as the HLB of surfactants became lower or more lipophilic. Radioactivity in the laminae and petioles of treated leaves was determined for both plants. The pattern of accumulation of  $^{14}\text{C}$  was similar in both plant tissues, but



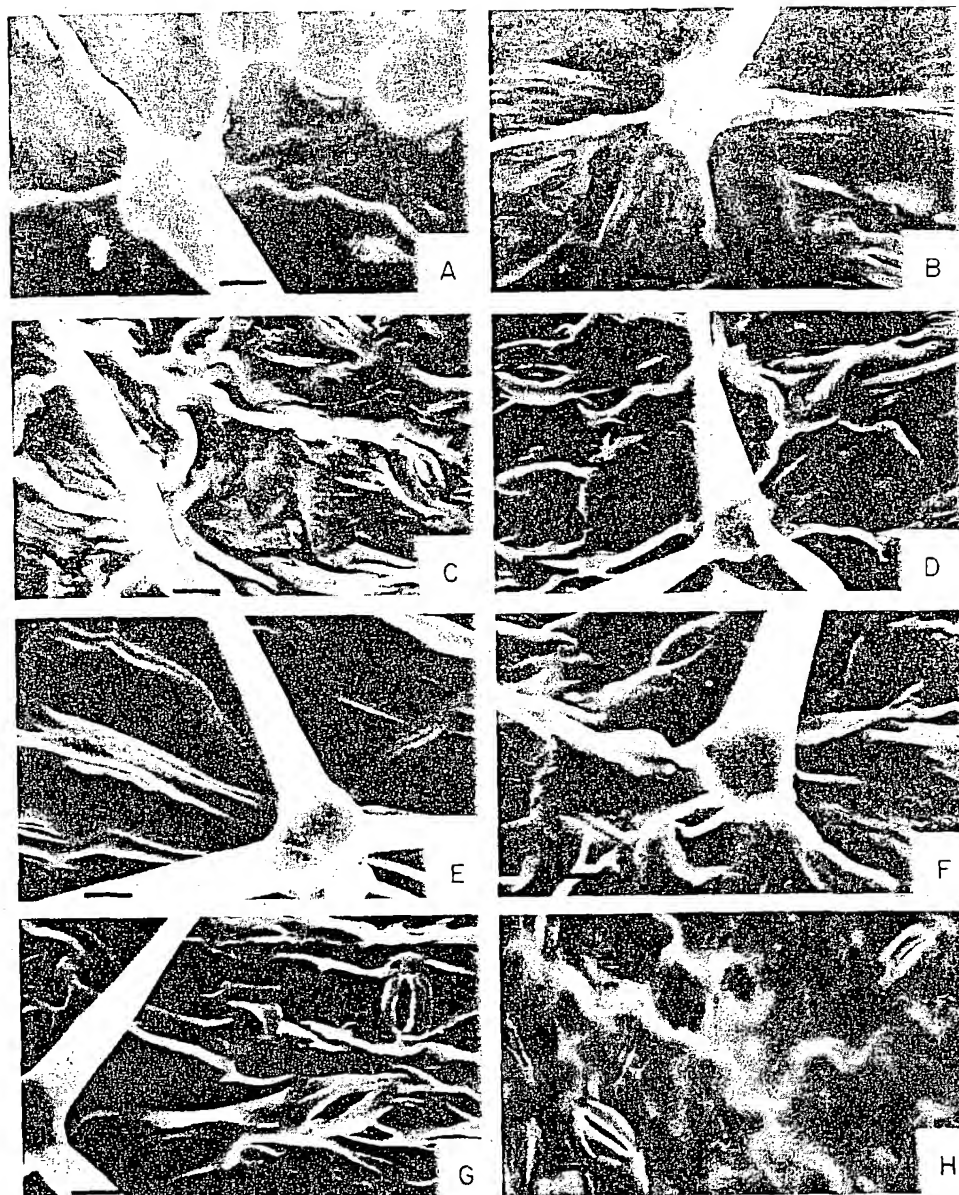


FIGURE 4. SEM micrographs of prickly sida leaf surfaces treated with 1% (w/w) surfactant solution. (A) Abaxial surface of leaf 3 h after dipping in surfactant (HLB 4.3) solution; (B) adaxial surface of leaf 72 h after dipping in the same solution; (C) adaxial surface of leaf 3 h after dipping in surfactant (HLB 8.0) solution; (D) abaxial surface of the same leaf; (E) adaxial surface of leaf 3 h after dipping in surfactant (HLB 12.0) solution; (F) adaxial surface 72 h after dipping in the same solution; (G) adaxial surface of leaf 72 h after dipping in surfactant (HLB 15.0) solution; (H) abaxial surface of the same leaf. Scale represents 10  $\mu$ .

the levels of radioactivity were much smaller in the petioles and significant differences were not observed among treatments. Therefore, only data for radioactivity in the laminae are presented (Tables 1 through 3). More  $^{14}\text{C}$ -activity in cotton leaves was associated with solutions containing the surfactant blend with HLB 8.0 in 82.5% methanol at each time

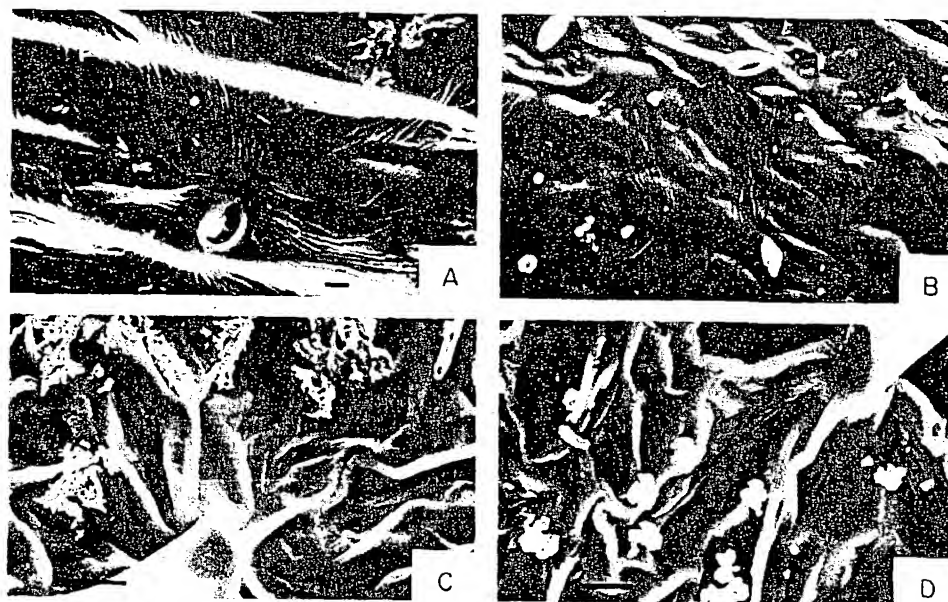


FIGURE 5. SEM micrographs of leaf surfaces treated with methazole. (A) Adaxial surface of cotton leaf 72 h after dipping in 0.8% (w/w) technical methazole-ethanol solution; (B) adaxial surface of cotton leaf 72 h after dipping in 1.0% (w/w) formulated methazole-distilled water solution; (C) adaxial surface of prickly sida leaf 72 h after dipping in 0.8% (w/w) technical methazole-ethanol solution; (D) adaxial surface of prickly-sida leaf 72 after dipping in 1.0% (w/w) formulated methazole-distilled water solution.

after treatment (Table 1). As the treatment time increased, radioactivity in the treated leaf increased except in the case of the surfactant with HLB 15.0 in 50% (v/v) methanol. Those increases were not statistically significant, however.

There were more distinct differences in the distribution of  $^{14}\text{C}$  in the treated leaf outside of the treated area among treatments in the case of prickly sida than in cotton despite less uptake in prickly sida (Table 1). Uptake of  $^{14}\text{C}$ -methazole was maximal with the 1% surfactant (HLB 4.3) — 99% methanol solution at each treatment time. These observations suggest that the mobility of  $^{14}\text{C}$ -methazole varies with plant species as well as the composition of the formulation.

In the previous experiment, the treatment solutions were prepared using methanol and aqueous-methanol solutions because of the low water solubility of  $^{14}\text{C}$ -methazole and Span 80 (HLB 4.3). In this experiment, the concentrations of methanol were adjusted to the same levels as in the previous experiment (Table 1), to examine the effect of methanol concentration alone and to compare its effect with that of surfactants plus methanol or aqueous methanol. Absorption and translocation of  $^{14}\text{C}$  increased slightly with increasing methanol concentration: up to 82.5%, with the maximum effect at 100% methanol for cotton and prickly sida (Table 2). The difference in  $^{14}\text{C}$  translocated when 100% methanol was employed, rather than other methanol concentrations of 40 to 82.5% (v/v), was remarkable for both species. These observations suggest that the addition of 17.5% (v/v) or more water to the treatment solution considerably reduces the effect of methanol on the uptake and translocation of  $^{14}\text{C}$ -methazole in both species.

In a third experiment,  $^{14}\text{C}$ -methazole was applied in solutions containing 1% surfactant and 99% methanol or in 100% methanol. The surfactants did not significantly increase the

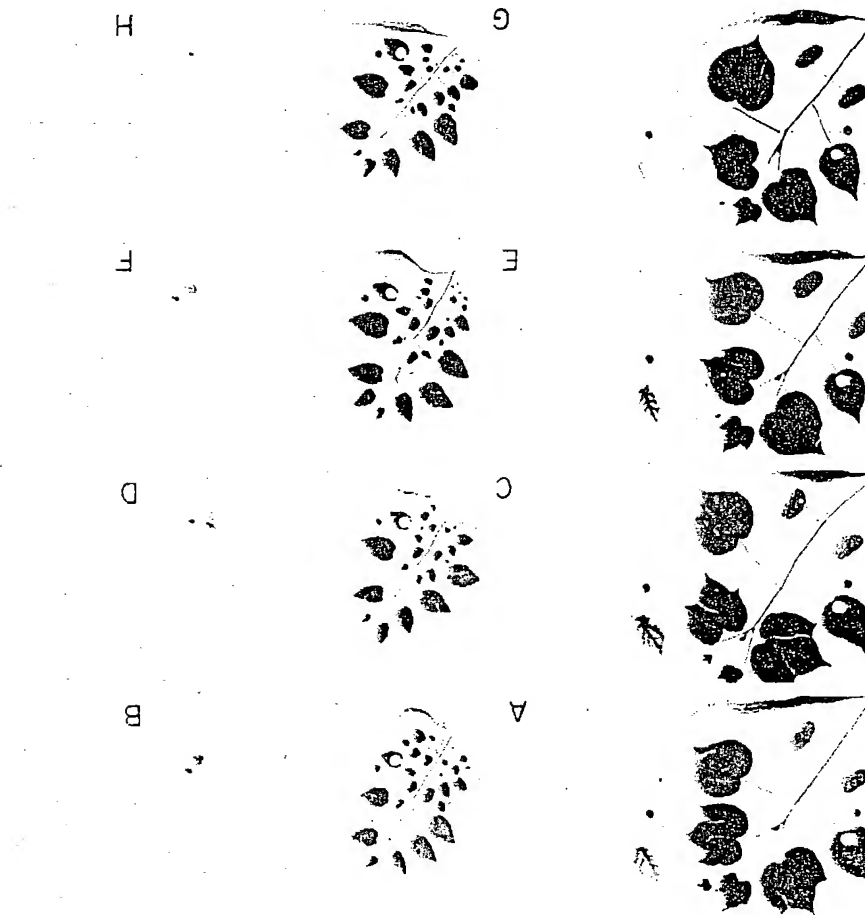


FIGURE 6. Accumulation of radioactivity after 72 h in cotton (left) and prickly sida (right) plants treated with 0.1  $\mu$ Ci of  $^{14}$ C-methazolin with 1% (w/v) polysorbate surfactant in methanol or methanol-aqueous solution. Plants (left: autoradiograms right: HLB of surfactant used and methanol content (% v/v) of treatment solutions, respectively) (A) and (B) 4.3, 99.0; (C) and (D) 8.0, 82.5; (E) and (F) 12.0, 64.0; (G) and (H) 15.0, 50.0.

accumulation of  $^{14}$ C outside of the treated areas in leaves of cotton after 72 h (Table 3). The methanol used in this experiment masked the effect of polysorbate surfactants as well as the effect of the HLB of these surfactants, suggesting that the effects seen in Figure 1 and Table 1 were methanol effects rather than HLB effects. In fact, polysorbate surfactant tended to restrict the influence of the 100% methanol solution on  $^{14}$ C-methazolin uptake in prickly sida (Table 3).  
 Autoradiograms (not shown) and quantitative data (not shown) indicated no distribution of  $^{14}$ C-fatty acid-labeled polysorbate surfactants in either species; no visible distribution of  $^{14}$ C occurred with any methanol concentration, any HLB of surfactants, or at any treatment time. Smith and Foy<sup>25</sup> reported similar observations on the movement of labeled polysorbate surfactants.  
 Because of the effect of 100% methanol on absorption and translocation, the effects of polysorbate surfactants themselves as well as their HLB effect were nullified when they were used in 100% methanol. Therefore, it is considered inappropriate to judge the effect

**TABLE 1**  
Accumulation of  $^{14}\text{C}$ -Methazole Outside the Treated Areas in Primary Leaves of Cotton and Fourth Leaves of Prickly Sida Following Application in 1% Surfactant Solutions Containing Various Amounts of Methanol

Species	Time after treatment (h)	Surfactant HLB and methanol content (v/v)			
		4.3, 99%	8.0, 82.5%	12.0, 64%	15.0, 50%
		10 <sup>3</sup> dpm			
Cotton	3	19.3 ab	21.8 ab	7.0 b	6.1 b
	24	28.9 ab	33.4 ab	17.8 ab	9.5 b
	72	34.6 a	39.6 a	22.5 ab	9.0 b
Prickly sida	3	2.4 cd	1.1 d	0.8 d	0.3 d
	24	6.3 ab	4.2 bc	2.0 cd	1.1 d
	72	8.2 a	6.5 ab	5.3 b	2.6 cd

Note: Means followed by the same letter within a species do not differ at the 5% level according to Duncan's multiple range test.

**TABLE 2**  
Accumulation of  $^{14}\text{C}$ -Methazole Outside the Treated Areas in Primary Leaves of Cotton and Fourth Leaves of Prickly Sida Following Application in Methanol or Aqueous Methanol

Species	Time after treatment (h)	Methanol content (% , v/v)				
		100.0	82.5	64.0	50.0	40.0
		10 <sup>3</sup> dpm				
Cotton	3	20.2 c	5.8 fg	7.1 fg	6.0 fg	4.5 g
	24	37.6 a	11.7 e-g	12.5 ef	10.6 e-g	9.8 e-g
	72	31.4 b	19.5 cd	13.5 c-f	10.4 e-g	15.5 c-e
Prickly sida	3	4.0 c	0.6 g	0.4 g	0.3 g	0.4 g
	24	7.4 b	0.8 fg	0.6 fg	0.4 g	0.5 g
	72	12.3 a	2.3 d	1.8 d	1.0 de	1.5 ef

Note: Means followed by the same letter within a species do not differ at the 5% level according to Duncan's multiple range test.

of the HLB of the surfactants by subtracting the value for the distribution of  $^{14}\text{C}$  with methanol alone from those for the distribution of  $^{14}\text{C}$  with surfactant and methanol. Figure 7 shows the results, with both plant species, of subtracting the value for the distribution of  $^{14}\text{C}$  with aqueous or absolute methanol from those for the distribution of  $^{14}\text{C}$  with polysorbate surfactants in the same solution. The HLB effects of polysorbate surfactants were similar in both plant species. The effect of surfactant was greatest with HLB 8.0 on the translocation of  $^{14}\text{C}$ -methazole in cotton plants. The plots below zero obtained at HLBs of 4.3 for both species are the result of the effect of 100% methanol being greater than 99% methanol plus surfactant. Also, the plots below zero obtained at HLB 15.0 for cotton are the result of 50% methanol being greater than 50% methanol plus surfactant. Thus, the method used (Figure 7) may not fully differentiate HLB effects. This method does, however, demonstrate consistent differences in the absorption and translocation of  $^{14}\text{C}$ -methazole that were correlated with HLB.



TABLE 3  
Accumulation of  $^{14}\text{C}$ -Methazole Outside the Treated Areas in Primary Leaves of Cotton and Fourth Leaves of Prickly Sida Following Application in Solutions Containing 1% Surfactant and 99% Methanol or in 100% Methanol

Species	Time after treatment (h)	Surfactant HLB				
		4.3	8.0	12.0 $10^3$ dpm	15.0	Methanol
Cotton	3	19.3 a	14.0 b	12.9 b	12.1 b	20.2 a
	24	28.9 a	35.3 a	31.8 a	22.6 a	37.5 a
	72	34.6 a	43.5 a	39.5 a	44.9 a	31.4 a
Prickly sida	3	2.4 ef	3.7 f	1.8 f	1.6 f	4.0 e
	24	6.3 cd	4.3 de	6.5 cd	3.7 e	7.4 c
	72	8.2 bc	7.3 c	7.5 c	9.4 b	12.3 a

Note: Means followed by the same letter within a species do not differ at the 5% level according to Duncan's multiple range test.

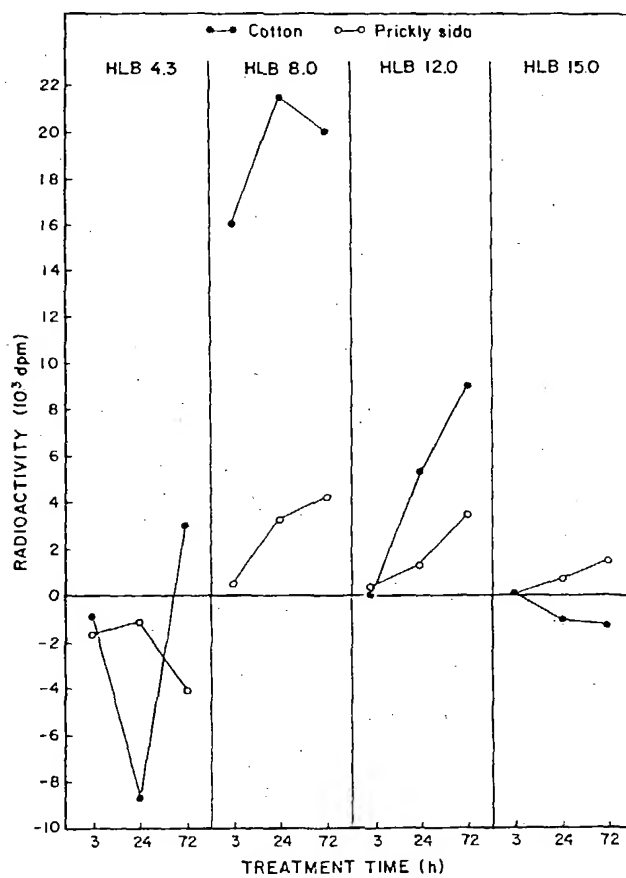


FIGURE 7. Influence of the HLB of polysorbate surfactants on absorption and translocation of  $^{14}\text{C}$ -methazole in the primary leaf of cotton and the fourth leaf of prickly sida plants.

### C. MOBILITY STUDIES IN SOIL

The degree to which soil adsorbed  $^{14}\text{C}$ -methazole when polysorbate surfactants were present is shown in Figure 8. All treatments showed the greatest amount of residue of  $^{14}\text{C}$ -methazole in the soil within the first 1 cm of depth. The amount of the residue decreased in proportion to the depth in the soil column, indicating that the herbicide remained predominantly in the top layers of the soil, as reported by other researchers.<sup>4,5,19,26</sup>

When methazole was applied with one fourth as much surfactant, approximately 85% of the total  $^{14}\text{C}$  applied was detected in the soil within 4 cm of the surface regardless of the HLB of the polysorbate surfactant used. The degree of  $^{14}\text{C}$  adsorption at the same soil depth decreased slightly with the increase of surfactant, while the radioactivity of the treatment with the  $^{14}\text{C}$ -methazole without surfactant was approximately 76% at the same soil column depth. However, approximately 96% or more of the radioactive material was determined in the soil within 7 cm in depth for all treatments; at this level, not only the HLB of the polysorbate surfactant, but also the polysorbate surfactant itself did not show any influence on the leaching of heterocyclic ring-labeled  $^{14}\text{C}$ -methazole.

When the ratio of the polysorbate surfactant and herbicide was the same, the influence of the HLB of the polysorbate surfactant was minimal. The results of the study on soil adsorption of substituted urea herbicides as influenced by surfactants showed that nonionic and anionic surfactants have either no effect or decrease the adsorption of these herbicides.<sup>2</sup> Bayer<sup>2</sup> reported that Tween 20 (nonionic surfactant containing polyoxyethylene sorbitan monolaurate, HLB 16.7) increased the leaching depth of diuron [*N*-(3,4-dichlorophenyl)-*N,N*-dimethylurea] by increasing the concentration of the surfactant.

Our results suggest that adsorption of  $^{14}\text{C}$ -methazole onto the soil surface was different from that of diuron. Why relatively low amounts of polysorbate surfactant restrict the movement of the herbicide more than greater amounts of the surfactant is not explained.

Koren et al.<sup>18</sup> reported that the movement of thiocarbamate herbicides was directly related to the water solubility of the herbicide and inversely related to the organic matter content of the soil. Our experimental results confirm this concept; the water solubility of methazole is 1.5 ppm at 25°C, and it was adsorbed on the soil in the top layers of the column. Tween 80 (HLB 15.0), a water-soluble surfactant, is used as a solubilizer in numerous industrial fields. However, even when methazole was applied with four times as much Tween 80, no significant difference in adsorption of  $^{14}\text{C}$  was observed, compared to the addition of the same amount of less water-soluble polysorbate surfactant.



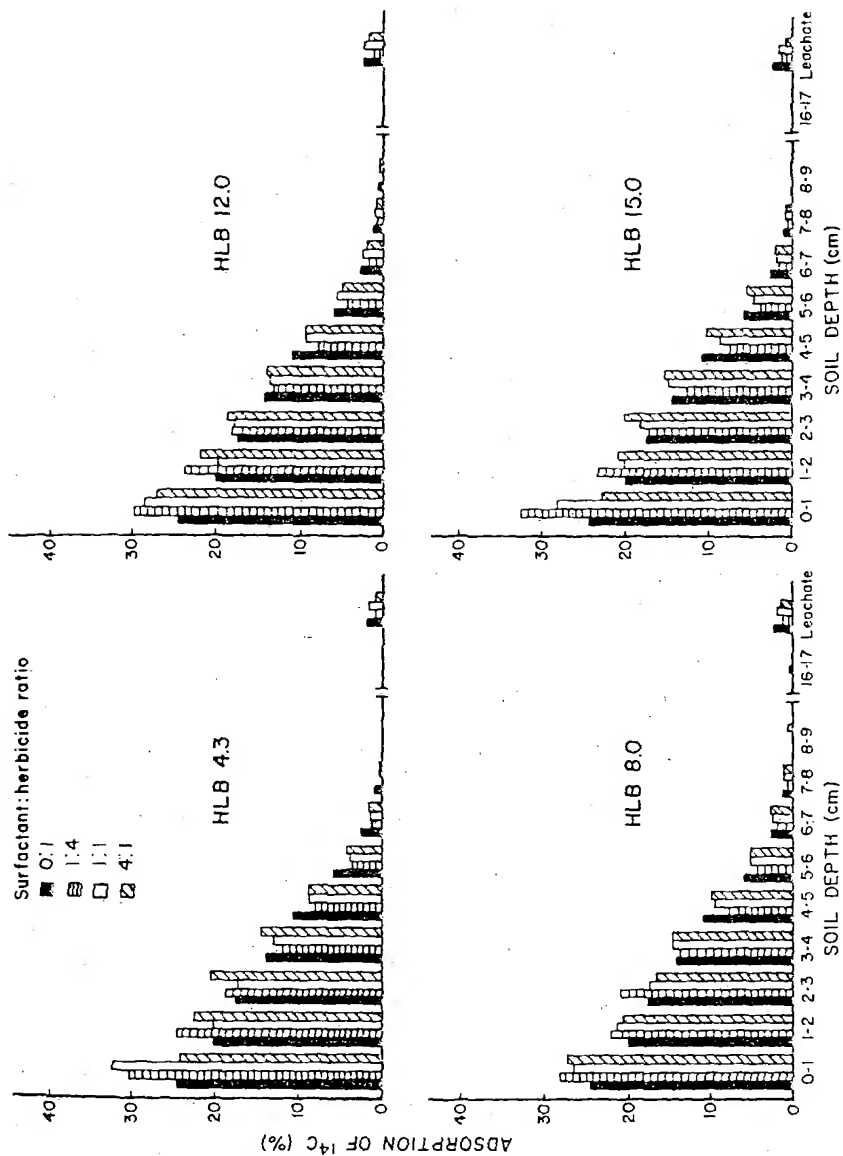


FIGURE 8. Influence of the amounts of surfactants with various HLB values on the leaching of <sup>14</sup>C-methazole, expressed as percent adsorption of <sup>14</sup>C-methazole on silt loam soil.

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## Chapter 15

CHLOROPHYLL FLUORESCENCE — A NONINVASIVE  
TECHNIQUE FOR RAPID INVESTIGATION OF THE EFFECTS  
OF ADJUVANTS ON HERBICIDE AND PLANT GROWTH  
REGULATOR UPTAKE BY LEAVES

Mick P. Percival, Mark H. Blowers, John W. Green and Neil R. Baker

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## ABSTRACT

Chlorophyll fluorescence measurements were used to investigate aspects of uptake by wheat leaves of the photosynthetically active herbicide diuron, the amino acid biosynthetic inhibitor herbicide glyphosate, and the plant growth regulator (PGR) chlormequat.

Quantitative changes in fluorescence, detected within 60 min of treatment, correlated directly with the concentration of diuron incorporated into leaf tissue. Subsequent fluorescence studies demonstrated that the formulation with Tween 20 enhanced diuron uptake. Further enhancement of diuron uptake by removal of the epicuticular wax layer was unaffected by Tween 20. Maximum uptake of diuron was achieved with Tween 20 concentrations near its critical micelle concentration (cmc) value. Fluorescence measurements were also used for the rapid selection of the most effective formulations of the photosynthetic herbicides (phenmedipham and bentazon) with commercial adjuvants.

Chlorophyll fluorescence emitted from young wheat leaves showed perturbation 24 h after treatment with the nonphotosynthetic herbicide glyphosate and the PGR, chlormequat. Rapid selection of the most effective adjuvant formulations of these compounds was also demonstrated using fluorescence measurements.

The results demonstrate that chlorophyll fluorescence measurements can be used to investigate and optimize herbicide and PGR uptake by leaves as well as for the rapid screening of different adjuvant formulations of herbicides and PGRs.

## I. INTRODUCTION

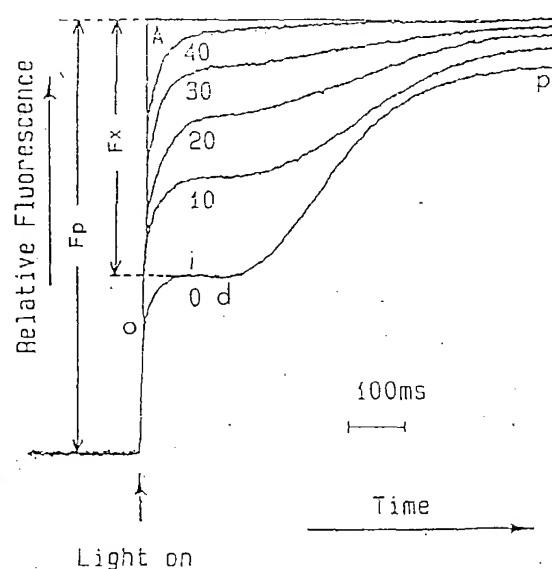
The use of adjuvants can improve the efficacy of herbicide and plant growth regulator (PGR) postemergent applications, often leading to significant gains both in the cost efficiency of the treatment and in diminished environmental impact. Yet, without quantitative *in vivo* probes of herbicide and PGR uptake, the effects of adjuvants are poorly understood and seldom fully optimized, since this often requires expensive and time-consuming field trials. It may be possible, however, to address many of these problems both rapidly and cost effectively using chlorophyll fluorescence measurements from treated leaves.

It is well known that chlorophyll fluorescence emission from photosynthetic tissues can be used as a noninvasive probe to monitor photochemical events *in vivo*.<sup>2</sup> For example, photochemical changes occurring in developing photosynthetic tissues and as a result of environmental stresses can be examined using fluorescence techniques.<sup>1,8,9</sup> Fluorescence analyses have also often been used to investigate the effects of herbicides on photosynthesis, particularly compounds which bind to the D1 protein of the photosystem 2 (PS2) reaction center.<sup>7</sup>

In this chapter, we demonstrate that chlorophyll fluorescence can be used to investigate aspects of herbicide uptake in leaves using the photosynthetically active herbicide, diuron [*N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea]. This technique enabled optimal adjuvant formulations of two other photosynthetically acting herbicides, phenmedipham {3-[(methoxycarbonyl)amino]phenyl(3-methylphenyl)carbamate} and bentazon [3-(1-methylethyl)-(1*H*)-benzo-thiadiazin-4(3*H*)-one-2,2-dioxide], to be selected. We also demonstrate how fluorescence techniques can be used to screen adjuvant formulations of the nonphotosynthetic herbicide, glyphosate[(*N*-phosphonomethyl)glycine], and the PGR, chlormequat (2-chloroethylmethyl-ammonium chloride).

## II. MATERIALS AND METHODS

Wheat (*Triticum aestivum* cv. Broom) seedlings were grown in controlled environment cabinets at 20°C under a mean photosynthetically active photon flux density (ppfd) of 250



**FIGURE 1.** Changes in chlorophyll fluorescence induction curves of a wheat leaf after treatment with 0.045 mM diuron are quantified using  $F_x/F_p$  or area ( $A$ ) over induction curve measurements.<sup>6</sup> Times after treatment are given in min.

$\mu\text{mol m}^{-2} \text{s}^{-1}$  and a 16-h photoperiod at constant relative humidity ( $RH = 70\%$ ). Seven-day-old (single-leaf stage) seedlings, selected for uniformity, were used in investigations with the herbicides diuron, phenmedipham, and bentazon. Eleven-day-old (two-leaf stage) seedlings were used in the chlormequat and glyphosate treatments. All seedlings were treated by total immersion of aerial tissue for 5 s in the herbicide and PGR formulations were described. Chlorophyll fluorescence was monitored, by methods previously described, from a 1-cm wheat leaf segment 2 cm from the tip of 6-d-old leaves and from a 3-cm leaf section located 9 cm from the base of the youngest leaf in 11-d-old seedlings.<sup>4,6</sup> Radiolabeled diuron incorporation was determined by scintillation after treatment of  $0.5 \text{ cm}^2$  of the 1-cm leaf segment of 6-d-old leaves with  $25 \mu\text{l}$  of  $^{14}\text{C}$ -diuron (2 mM), followed by extraction into 2 ml of ethanol after chlorophyll fluorescence had been measured. Epicuticular wax was removed from leaves by the application and subsequent stripping of a cellulose acetate (4%, w/v) film.

### III. RESULTS AND DISCUSSION

Most chlorophyll fluorescence emission is derived from excited chlorophylls associated with PS2 complexes in chloroplast membranes. Upon illumination, dark-adapted leaves exhibit a rapid induction of fluorescence which primarily reflects initial photochemical events associated with PS2 (see curve for 0 min, Figure 1). The rapid fluorescence induction has been described by the nomenclature o, i, d, and p (Figure 1).<sup>5</sup> The minimal fluorescence level attained when PS2 is maximally oxidized in nonenergized membranes is represented by o. The i-d inflection and the level of fluorescence at  $F_i$  correlate with the redox state of the primary quinone electron acceptor ( $Q_A$ ) in PS2. The rise to p and fluorescence level at  $F_p$  are governed by reduction of the plastoquinone (PQ) pool (secondary electron acceptor) and energization of the thylakoid membrane.<sup>5</sup> Perturbation of PS2 photochemistry will result in changes in these fluorescence parameters, which can be quantified by the ratio  $F_x/F_p$



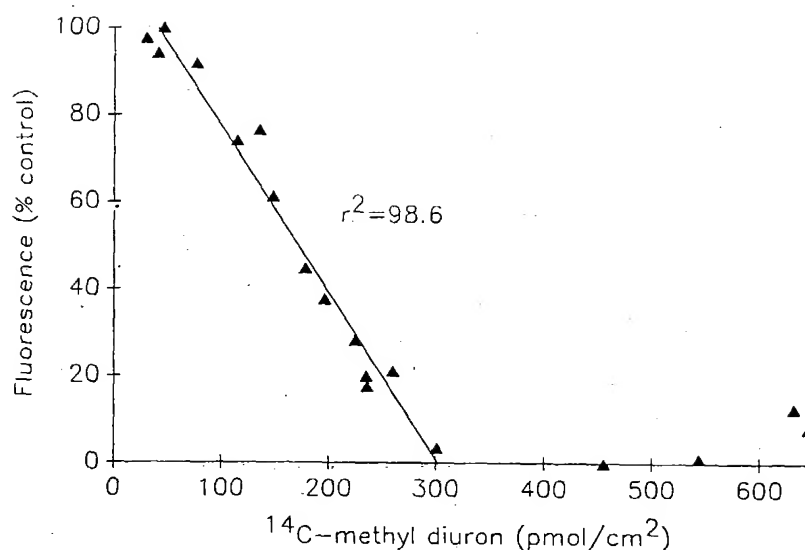


FIGURE 2. Correlation between posttreatment changes in fluorescence ( $F_x/F_p$ ) and  $^{14}\text{C}$ -diuron uptake (expressed on a leaf area basis).

$[(F_p - F_i)/F_p]$  (Figure 1).<sup>4</sup> Any herbicide and PGR effects on PS2 photochemistry and fluorescence are most likely to result from perturbation of photosynthetic electron transport and thylakoid energization and/or impairment of development and repair of photosynthetic membrane components involved in these processes.

The rapid effect of the photosynthetically active herbicide diuron on fluorescence induction in wheat leaves is shown in Figure 1. The response is typical of herbicides which inhibit PS2 photochemistry by binding to the PS2 reaction center D1 polypeptide, preventing electron transfer to PQ and reoxidation of  $Q_A$ . Simultaneous fluorescence and  $^{14}\text{C}$ -diuron incorporation measurement (Figure 2) indicate that uptake of diuron into the leaves correlates with the fluorescence changes generated. This may result from the fluorescence effect being directly related to diuron binding to the D1 polypeptide, which will be determined by the relative uptake of herbicide. Consequently, fluorescence measurement can be used for the rapid estimation of diuron uptake into leaves and to investigate factors which influence herbicide penetration.

It is well known that the formulation of herbicides with adjuvants can markedly facilitate uptake;<sup>3</sup> however, with few *in vivo* probes of herbicide penetration, the processes involved are neither well understood nor fully optimized. Enhanced herbicide uptake was indicated by a greater fluorescence response from leaves treated with diuron formulated with 0.1% (v/v) Tween 20 (Figure 3). Tween 20 by itself (and other adjuvants used in this study) had no effect on fluorescence emission (data not shown). Removing the leaf epicuticular wax layer resulted in a greater fluorescence response, which was not affected by the inclusion of Tween 20 (Figure 3). These fluorescence results clearly identify the epicuticular wax layer as the major site of resistance to the uptake of diuron and demonstrate that Tween 20 interacts only with this layer when promoting herbicide uptake.

The fluorescence response of leaves treated with diuron was also found to be dependent on the Tween 20 concentration (Figure 4). The maximum effect was observed using approximately 100 mg/l of Tween 20, close to its cmc (Figure 4). Above the cmc, the concentration of the monomeric form of the adjuvant is maximally maintained, suggesting

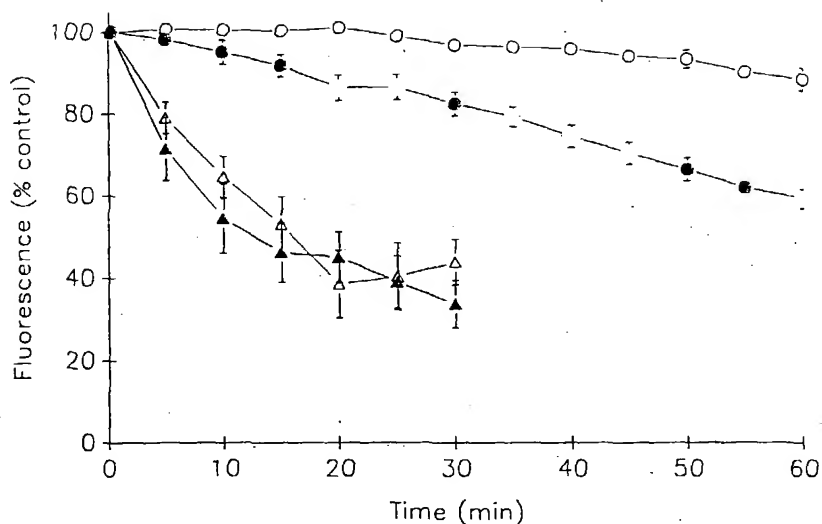


FIGURE 3. Posttreatment changes in the fluorescence induction parameter ( $F_x/F_p$ ) from wheat leaves treated with diuron (○) and diuron + 0.1% (v/v) Tween 20 (●), and leaves with their wax layer removed and treated with diuron (▲) and diuron + 0.1% (v/v) Tween 20 (△).

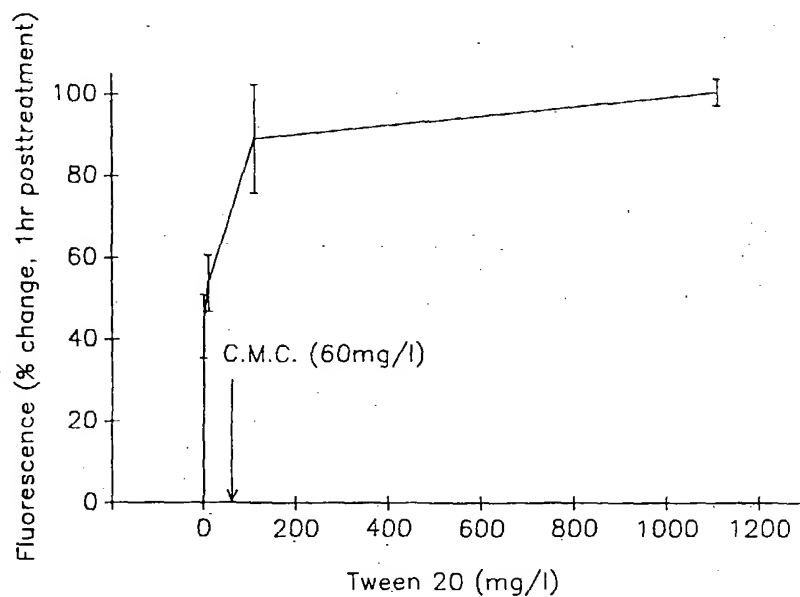


FIGURE 4. Changes in the fluorescence parameter ( $F_x/F_p$ ) measured from leaves 1 h after treatment with diuron formulated with a range of Tween 20 concentrations.

that the adjuvant is probably most effective at facilitating diuron uptake in its monomeric form. The results also demonstrate that fluorescence measurement can be used for the rapid determination of effective adjuvant concentrations.

Leaves treated with formulations of the PS2 herbicides, phenmedipham (Betanal-E) and bentazon (Basagran), with water and the commercially available adjuvants, Actipron (mineral

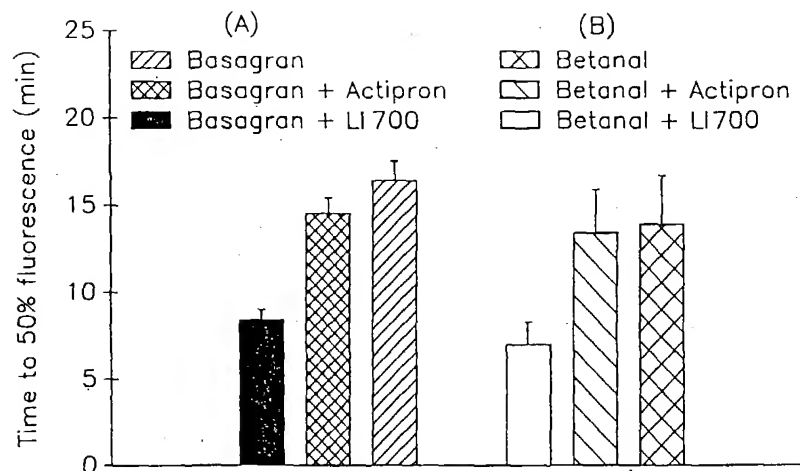


FIGURE 5. Comparison of the effects of (A) water, Actipron (2.5%, v/v), and LI 700 (0.5%, v/v) formulations of Betanal-E [a.i.] (active ingredient) phenmedipham, 1.425 mg/ml and (B) water, Actipron (1.0%, v/v), and LI 700 (0.5%, v/v) formulations of Basagran (a.i. bentazone, 9.6 mg/ml) on fluorescence emission from treated leaves as estimated from the time to achieve 50% reduction in  $F_x/F_p$ .

oil) and LI 700 (acidified soya lecithin), also exhibited different fluorescence responses indicative of different herbicide uptake rates (Figure 5). The most rapid fluorescence responses showed that LI 700 was the most effective with both herbicides at enhancing uptake. The results also demonstrate that these fluorescence kinetics can be employed to monitor the penetration of any herbicide which affects PS2 photochemistry directly.

Changes in the fluorescence emission from immature wheat leaves were also found to relate to the application dosage of the nonphotosynthetic herbicide, glyphosate (unpublished data), and the PGR, chlormequat.<sup>7</sup> These responses were determined 24 h after treatment and were possibly due to some impairment of the development of fully competent photosynthetic membranes in younger tissues.<sup>7</sup> Consequently, it was also possible to screen different formulations of these chemicals with the commercial adjuvants Ethokem, Agral, and LI 700, using fluorescence. Glyphosate effects were most enhanced by Ethokem, whereas LI 700 promoted the most uptake of chlormequat (Figure 6).

In conclusion, despite the need for further investigations to confirm and correctly interpret many of the observations relating to fluorescence changes, these preliminary studies do indicate that chlorophyll fluorescence has potential for use as a rapid, sensitive, noninvasive probe for monitoring factors affecting herbicide and PGR uptake and activity in intact leaves. The technique would also appear to have application for the rapid screening of effective field herbicide and PGR adjuvant formulations.

### ACKNOWLEDGMENT

Some of the fluorescence data are reproduced with the kind permission of Newman Agrochemicals Ltd., Barton, Cambs. CB3 7AR, U.K.

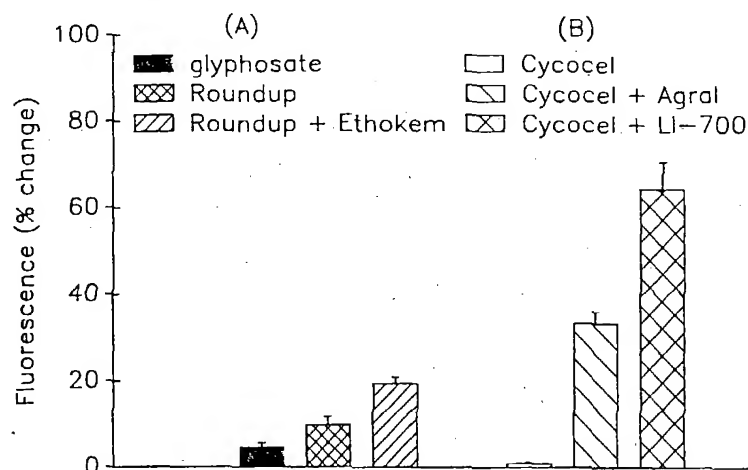


FIGURE 6. Comparison of (A) the effects of glyphosate (3.35 mg/ml), Roundup® (active ingredient [a.i.] glyphosate, 3.35 mg/ml), and Roundup® + 0.5% (v/v) Ethokem, and (B) Cycocel (a.i. chlormequat, 8.04 mg/ml), Cycocel + 0.025% (v/v) Agral, and Cycocel + 0.5% (v/v) LI-700 on fluorescence (Fx/Fp) emission from immature wheat leaves 24 h after treatment.

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## Chapter 16

**PHOTODEGRADATION AND ABSORPTION OF SETHOXYDIM  
AS ADJUVANT-INFLUENCED SURFACE EFFECTS**

James L. Hazen and Philip J. Krebs

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## ABSTRACT

Experimental adjuvants were tank mixed with sethoxydim {2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one} and tested on glass slides and whole plants to evaluate their influence on herbicide photodegradation and absorption, respectively.

Adjuvant materials were classified relative to their effect on sethoxydim half-life when exposed to photodegradation conditions in a temperature-controlled ORIGINAL HANAU Suntest Apparatus. Studies on seedling corn (*Zea mays* L.) identified adjuvant materials which greatly enhanced the absorption of sethoxydim from a controlled application of tank mix to the leaf surface.

The standard crop oil concentrate was shown to greatly enhance the rate of sethoxydim degradation on glass.

A superior adjuvant for sethoxydim was formulated from materials thus identified. In addition, certain of these materials were incorporated into new ready-to-dilute (RTD) formulations which contain herbicide and adjuvant.

## I. INTRODUCTION

It is well established that adjuvants play an important role in the application of herbicides. Experience shows that successful weed control results when the appropriate adjuvant and herbicide combination are properly applied to the target. An appropriate adjuvant is one which has been selected on its ability to consistently meet the needs of the herbicide formulation with which it is co-applied.

Such needs include physical, chemical, and/or biological modifications. Physical and chemical uses for adjuvant materials are related to sprayability, compatibility, and other water-quality influences. There are many nuances of biological improvement via adjuvants. Some result from consideration of the previous chemical and physical problems, while others result directly from the effect of the application on the target.

In most cases, commercial adjuvants were developed to improve the physical appearance of the spray solution (dense, white emulsion of paraffinic oil) without having a specific pesticide formulation or active ingredient in mind. With few exceptions, oil concentrates are not regulated for activity, compatibility, or consistency of composition. Finding the appropriate adjuvant is unlikely to happen without a serious investigation.

Interest in developing a superior adjuvant system began with the realization that we could not control the quality of crop oil concentrates on the market and that, with the proliferation of such adjuvants, it would be impossible to test and maintain a list of acceptable adjuvants for use with products such as Poast Herbicide®\* (sethoxydim).

Examining the adjuvant needs of BASF herbicides required the design of a program to identify adjuvant materials for specific targets and later to evaluate their effect on the herbicide as well as the target. Certain aspects of this research have been previously reported.<sup>1-4</sup>

As the biochemical optimization of our sethoxydim formulation was approached, obvious differences in adjuvant performance between greenhouse and field trials became a concern.

If a population of plants is treated and half of them are placed outside in the direct sunlight while the other group is kept in the greenhouse under similar environmental conditions, except for the lack of UV light, the effect of the UV light exposure can be observed as differences in plant injury.

In the greenhouse, 100 g/ha sethoxydim is active across a variety of species. The activity drops off dramatically on the plants placed outside, especially corn. The investigation to explain these indoor/outdoor performance variations is the basis of this chapter.

\* Poast Herbicide is a registered trademark of BASF AG.



## II. MATERIALS AND METHODS

### A. TEST MATERIALS

Poast Herbicide, Lot SP4040, was used as the source of sethoxydim for glass slide and whole plant studies. Dash Adjuvant\*, Lot 86-5, and AGWAY BOOSTER Plus E (no lot number) were used as the standard adjuvants. World Health Organization (WHO) standard 342 ppm synthetic hard water was used as diluent.

Adjuvants were examined as coded materials, identified with BCH . . . S numbers. Many of the tested materials were previously identified in the references as surfactants from series A, B, C, or D, having a subsequent one- or two-digit number (e.g., Surfactant D-7, which later became BCH 815 00S).

### B. TEST SOLUTIONS

The tank-mix solutions in the glass slide test were prepared as 0.5 g of Poast Herbicide with 2.5 g of adjuvant brought with acetone to a 100-ml volume in a Class A volumetric flask. This yields a sethoxydim concentration of 1.12 mg/ml, which corresponds to a use rate of 1.17 l/ha of Poast Herbicide with 5.85 l/ha of adjuvant in 187 l/ha of spray solution (1 pint of Poast with 2.5 qt of adjuvant in 20 gal/acre). This adjuvant rate was a bit high; however, the interest was in optimal adjuvant use rates for maximum adjuvant effect. Greater and/or lesser adjuvant rates were examined for certain materials. Solutions were transferred into amber glass bottles for storage.

Tank-mix solutions for the whole plant study were prepared by weighing approximately 0.5 g of Poast Herbicide, Lot SP4040, into a 100-ml Class A volumetric flask, adding 20 ml of water, and mixing prior to adding the adjuvant material, which was weighed (varied amounts, proportional to composition in blend or to field use rate) into the flask and then brought to volume with additional 342 ppm hard water. The content was then transferred to an 118-ml amber bottle to protect the sample from light.

### C. ANALYTICAL METHOD

HPLC analysis was accomplished on a REGIS 5- $\mu$  ODS-II, 25 cm  $\times$  4.6 mm column, with a mobile phase (80:19:1) of acetonitrile, water, and acetic acid, flowing at 1.0 ml/min. The result of a 250- $\mu$ l injection was detected at a wavelength of 280 nm.

The standard solutions of sethoxydim were prepared by weighing 100.9 mg of 9.9% sethoxydim (active ingredient) weighed into a 250-ml Class A volumetric flask, thus having a concentration of 0.040 mg/ml. A standard curve was generated from dilutions of this stock solution (e.g., 10 ml into 100 was 0.0040 g/ml, and additional stock solution dilutions were 8, 5, 3, and 1 ml into 100 ml, yielding respective concentrations of 0.004 to 0.0004 mg/ml).

### D. GLASS SLIDE STUDY

A study of sethoxydim on glass slides was designed to provide information about the effect of adjuvant materials on the rate of photodegradation.

Glass microscope slides were spotted by syringe with 10  $\mu$ l of test solution applied as a single spot. Treated slides were then exposed for increments of 0, 1, 2, 3, 4, 5, 10, 15, 20, 30, and 40 min. The ORIGINAL HANAU Suntest Apparatus\*\* was operated with cooling to the tray to maintain a surface temperature of 28°C. The fan was on and the energy output level of the lamp was not observed to vary over the test period. Preliminary studies

\* Dash Adjuvant is a registered trademark of BASF Corporation.

\*\* DSET Laboratories Inc., Phoenix, AZ 85027.

in the Suntest Apparatus had been conducted to determine the effects of fan, cooling to tray, and exposure time.

Due to limited space on the Suntest tray and the need to compare multiple solutions concurrently, there could be only one slide per tank mix per time interval. Over the course of the entire study, several tank mixes were repeated with very similar results.

At  $t_0$ , 10  $\mu$ l of test solution was transferred onto a glass slide which was then rinsed with 3.0 ml of acetonitrile into a scintillation vial. At each appropriate interval, the slides were individually rinsed with 3.0 ml of acetonitrile, recycled a number of times over the slide surface to ensure adequate flushing of the tank-mix residue into the collection container. The efficiency of glass slide rinsing had been investigated by comparing the sethoxydim rinsing efficiency of ethyl acetate, isooctanol, dimethyl ketone, methanol, and acetonitrile. The latter removed the most sethoxydim and was used for these studies.

Residue collected in this rinsate was directly assayed for sethoxydim. This was possible since the rinse volume and initial sethoxydim applied combined to bring the concentration above the lower detection limit for the analytical method employed. As the mobile phase was 80% acetonitrile, direct injection did not disturb system equilibrium.

Analytical values were normalized against the recovery of sethoxydim from a treated, non-UV-exposed slide. During preliminary studies, attempts were made to incorporate an internal standard to assist with the accurate quantification of sethoxydim; however, thymol did not adequately rinse from the slide due to limited solubility in isooctane, and dipropyl phthalate was noted to decompose when exposed to sunlight. Since the thymol and dipropyl phthalate internal standards had proved to be unreliable, correlation was made to a nonsunlight-exposed, zero-time slide application of the appropriate tank mix.

It was noted that a solvent (Aromatic 150 — EXXON), detectable under the stated chromatographic conditions, was interfering with the  $t_0$  samples since it did not have time to evaporate prior to sample work-up. Nitrogen was used to gently blow dry the  $t_0$  slides. This removed the interfering solvent and was shown not to cause detectable degradation of sethoxydim.

#### E. WHOLE PLANT STUDY

These studies determined the amount of applied sethoxydim that can be recovered from the surface of a corn plant leaf at increasing time intervals after application of a solution containing a known amount of sethoxydim. (The amount of sethoxydim recovered subtracted from the initial 100% equals the absorbed sethoxydim which is no longer at the leaf surface.)

A preliminary study of sethoxydim on corn leaf surfaces was accomplished to determine the length of exposure time, relative rate of uptake, and leaf rinsing procedures. Some attention was given to confirm that significant sethoxydim decomposition products were not generated in the growth chamber since decomposition had been noted on plants placed outdoors.

Greenhouse-grown corn (Pioneer 3320) plants, ranging from 15 to 23 cm (6 to 9 in) tall at 10 to 12 d after planting (DAP), were used as test specimens. Plants were grown in a 1:1 blend of Norfolk sandy loam/Metro 360\* organic medium, amended with lime and fertilizer at agricultural field rates. Light intensity in the greenhouse for initial growth ranged from 240 to 530  $\mu$ E M<sup>-2</sup> s<sup>-1</sup> for supplement light and sunlight (mid-September), respectively. The plant population in 8.2-cm-diameter pots was reduced to one per pot by severing all others at the soil surface before transferring to the growth chamber. The test plants were allowed to acclimate to the growth chamber conditions for 24 h before treatment. Growth chamber conditions were adjusted to less than optimal conditions (20°C and 50% relative humidity rather than the normal 25°C at 85% RH) to encourage expression of adjuvant

\* Product of W. R. Grace, Horticultural Products, Cambridge, MA.

TABLE 1  
Percent of Initial Sethoxydim Recovered from Glass Slide Surface After  
28°C Suntest UV Exposure

Adj.:Seth. ratio	Adjuvant description	Exposure interval (min)									
		1	2	3	4	5	10	15	20	30	40
0:1	None	80	57	47	31	26	14	6	5	—	—
2.50:1	Dash	83	73	60	52	48	24	13	8	—	—
2.50:1	COC	77	63	47	34	30	8	5	0	—	—
1.88:1	BCH 815 00S	76	57	45	35	29	16	8	5	2	0
0.94:1	BCH 828 00S	78	63	50	37	33	16	8	7	0	0
0.94:1	BCH 826 00S	86	72	59	45	36	26	16	10	7	6
0.38:1	BCH 834 00S	85	77	67	60	57	42	30	25	6	4
0.25:1	BCH 836 00S	89	80	69	59	58	41	30	22	13	8
2.50:1	BCH 779 00S	74	53	37	34	18	5	0	0	—	—

effects. Growth chamber light (continuous) was from incandescent and fluorescent sources; the light energy at bench height was measured as  $175$  to  $200 \mu\text{E M}^{-2} \text{s}^{-1}$  with no measurable UV component.

Normal application of a  $10\text{-}\mu\text{l}$  test solution onto the horizontal adaxial leaf surface was accomplished as 20 spaced droplets using a Hamilton repeating dispenser (micropipetter) fitted with a Hamilton  $10\text{-}\mu\text{l}$  syringe.

At  $t_0$ ,  $10 \mu\text{l}$  of test solution was spotted onto the leaf surface and immediately rinsed with  $3.0 \text{ ml}$  of acetonitrile, recycled into a scintillation vial. Two plants were used for each tank-mix time interval. Sethoxydim recovery from intervals of 0.25, 1, 2, 3, 4, 5, and 7 h were normalized to the  $t_0$  recovery value.

### III. RESULTS AND DISCUSSION

#### A. GLASS SLIDE STUDY

Sethoxydim is a very photolabile material, but it is not the only compound with this sensitivity. The half-lives for sethoxydim and many other postemergence graminicides are within the 45- to 180-min range.

We examined the degradation of sethoxydim on glass slides under a nonfiltered UV lamp. In an ORIGINAL HANAU Suntest Apparatus, the half-life of sethoxydim is about 9 min. With the 300-nm cutoff filter in place, the UV energy in this test system is reported to represent the intensity of the sun at noon on the equator. In the real world, the actual half-life is longer, but still short enough to become a major concern.

The first slide study compared the relative rate of sethoxydim decomposition, as Poast Herbicide alone, with Dash Adjuvant, crop oil concentrate (ICI — AtPlus 411F-type), and methylated sunflower oil. In Table 1, most obvious is the fact that crop oil concentrate (COC) and methyl-sunflower oil accelerate the photodecomposition of sethoxydim, while Dash has a minimal effect.

This test also examined the effect of individual components of Dash in the proportions in which they are used in Dash Adjuvant. It can be seen that 834 and 836 improved the stability of sethoxydim, while 815 and 779 slightly increased the rate of decomposition.

In Table 2, the effect on sethoxydim stability from the increase or decrease of an individual Dash component was evaluated. Increasing 834 had no effect, but decreasing 834 slightly reduced the recovery of sethoxydim. There was no improvement in sethoxydim recovery from changing the 836 content. Certain other materials were shown to have a

TABLE 2  
Percent of Initial Sethoxydim Recovered from Glass Slide Surface After  
28°C Suntest UV Exposure

Adj.:Seth. ratio	Adjuvant description	Exposure interval (min)									
		1	2	3	4	5	10	15	20	30	40
0:1	None	88	81	71	62	59	46	32	20	16	9
5:1	Dash	86	80	67	61	58	40	29	21	11	6
5:1	COC	75	62	50	35	29	10	5	0	0	0
0.38:1	BCH 834 00S	89	78	71	62	55	42	34	24	15	9
0.25:1	BCH 834 00S	87	79	66	58	56	37	21	12	11	8
1.00:1	BCH 834 00S	87	80	71	61	58	45	31	23	15	9
0.25:1	BCH 836 00S	87	76	65	54	52	34	25	16	12	7
0.13:1	BCH 836 00S	87	77	66	55	57	31	22	13	8	5
1.00:1	BCH 836 00S	87	—	66	52	50	41	23	16	9	5
0.25:1	BCH 836 05S	81	78	64	57	52	38	27	19	12	7
0.25:1	BCH 770 00S	88	78	63	57	55	37	20	11	8	6
0.94:1	BCH 828 00S	79	69	51	42	32	19	9	4	0	0
0.50:1	BCH 890 00S	87	80	67	58	51	40	27	16	9	5
0.50:1	BCH 842 00S	86	77	67	58	55	39	29	20	12	9
0.50:1	BCH 843 00S	89	81	72	62	60	45	31	19	12	7

TABLE 3  
Percent of Initial Sethoxydim Recovered from Glass Slide Surface After 28°C  
Suntest UV Exposure

Adj.:Seth. ratio	Adjuvant description	Exposure interval (min)									
		1	2	3	4	5	10	15	20	30	40
0:1	None	88	81	71	62	59	46	32	20	16	9
5:1	COC	75	62	50	35	29	10	5	0	0	0
5:1	Dash	86	80	67	61	58	40	29	21	11	6
5:1	Dash	87	79	68	59	55	32	22	13	8	4
5:1	Methyl Sunflowerate	79	67	52	42	35	21	9	5	0	0
0.5:1	Methanol	88	80	68	63	54	39	21	12	10	3
0.5:1	<i>n</i> -Octanol	93	81	73	66	57	46	35	26	17	7
0.5:1	<i>t</i> -Butanol	87	79	64	59	55	41	26	17	6	5
0.5:1	<i>p</i> -Aminobenzoic acid	93	90	79	69	74	55	45	37	29	18
0.5:1	Propionic acid	85	81	67	56	52	36	26	16	7	5
0.5:1	Benzoic acid	89	83	72	67	62	47	46	20	13	11
0.5:1	$\alpha$ -Tocopherol acetate	84	74	57	45	40	38	20	12	8	4
0.5:1	Ascorbyl palmitate	91	86	76	70	68	57	41	38	21	19
0.5:1	Ascorbic acid	91	84	76	70	66	51	42	29	20	15
0.25:1	Uvinul D-49	95	94	88	81	78	61	57	48	29	25
1.00:1	Uvinul D-50	97	94	94	90	87	84	76	69	58	51
0.50:1	Uvinul D-50	97	94	92	88	85	79	74	69	60	55
0.05:1	Uvinul D-50	93	92	85	79	76	66	66	35	33	32
0.01:1	Uvinul D-50	92	83	81	72	71	53	45	33	21	13

similar effect on the degradation of sethoxydim and could possibly function as alternate components.

In the next series, several UV absorbers, alcohols, and antioxidants were checked at rates equal to 10% of the nominal adjuvant composition. Table 3 presents data to indicate that UVINUL®\* D-50, PABA, and ascorbyl palmitate improved the UV stability of se-

\* UVINUL is a registered trademark of BASF AG.

TABLE 4

Percent of Initial Sethoxydim Recovered from Glass Slide Surface  
After 28°C Suntest UV Exposure. Effect of 300-NM Cutoff Filter

Adj.:Seth. ratio	Adjuvant description	Exposure interval (min): filter/no filter*					
		1	3	5	10	20	30
0:1	None	97/89	92/71	89/58	81/43	71/18	64/12
5:1	Dash	94/87	89/68	84/55	73/32	57/13	43/8
1.88:1	BCH 815 00S	97/81	90/57	85/41	74/28	58/6	43/5
0.38:1	BCH 834 00S	96/91	92/76	89/70	81/57	74/38	63/27
0.25:1	BCH 836 00S	96/92	94/83	90/75	80/56	71/41	62/30
2.50:1	BCH 779 00S	94/86	91/69	87/59	80/45	73/21	63/16

\* Data generated with/without 300-nm UV cutoff filter in Suntest apparatus.

thoxydim;  $\alpha$ -tocopherol acetate did not. These responses indicate that the decomposition mechanism is not related to steric hindrance or amphipaths. Antioxidants and UV inhibitors significantly retard the photodegradation of sethoxydim.

Table 4 contrasts the effect of various adjuvant components on sethoxydim stability when the Suntest Apparatus is operated with a 300-nm cutoff filter in place, compared to the norm for this study which did not employ this filter. The energy below 300 nm obviously accelerates sethoxydim decomposition. This indicates that the actual rate of decomposition is substantially less than the nonfiltered data would suggest. Sethoxydim surface degradation by UV light is actually enhanced by COC.

#### B. WHOLE PLANT STUDY

Two major events occur once the spray droplets have been applied to the target surface: photodegradation and uptake. We have uptake removing herbicide from the leaf surface and photodegradation decomposing the herbicide which remains on the surface. The longer the herbicide remains at the surface, proportionately less potential activity remains for uptake. This reduces the chance for a weed to absorb the lethal dose needed for control.

Two options are available: protect the active ingredient on the surface with a suitable UV protectant and/or increase its rate of uptake by the plant. It is important to get the herbicide into the plant as quickly as possible. The cuticle is known to protect the plant against the effects of UV light; it will do the same for a herbicide that has penetrated the cuticle.

Whole plant studies examined the effect of adjuvants on the absorption of sethoxydim by corn plant leaf. The sethoxydim applied minus the sethoxydim recovered from the leaf surface suggests the amount of sethoxydim absorbed (and/or decomposed).

As shown in Table 5, recovery of sethoxydim from the surface levels out after 3 h, indicating a very slow rate of uptake from the Poast Herbicide formulation applied without any adjuvant. After 7 h, 40% of the initial sethoxydim was left on the surface and significant degradation products were noted. COC improved the rate of sethoxydim uptake, but was no match for Dash Adjuvant. Methylated sunflower oil increased the uptake about as much as BCH 815 00S. BCH 834 00S had significant uptake enhancement, but less than BCH 815 00S.

The last study in this series presents, in Table 6, the sethoxydim absorption for Poast Herbicide when tank mixed with oil concentrate (0.9 l) or with Dash (0.9 l), compared to the adjuvant-containing Poast Plus® Herbicide\* formulation. Poast alone and a 120 g/l

\* POAST PLUS Herbicide is a trademark of BASF Corporation.



TABLE 5  
Percent of Initial Sethoxydim Recovered from Surface of Corn  
Leaf After 20°C Growth Chamber Exposure

Adj.:Seth. ratio	Adjuvant description	Exposure interval (h)						
		0.25	1	2	3	4	5	7
0:1	None	82	74	61	50	53	53	44
2.50:1	Dash	67	24	8	0	0	0	0
2.50:1	COC	81	62	36	24	8	10	4
0:1	None	87	73	65	60	54	55	39
1.25:1	BCH 815 00S	80	22	8	7	6	0	0
1.25:1	BCH 834 00S	87	77	53	49	37	20	12
0:1	None	90	79	64	62	51	44	42
1.25:1	BCH 836 00S	83	63	23	9	5	0	0
1.25:1	BCH 779 00S	91	82	67	58	52	38	24
0:1	None	91	86	77	73	64	59	45
12.5:1	BCH 778 00S	54	42	39	43	40	26	27
2.50:1	Methyl Sunflowerate	79	46	13	8	6	0	0

TABLE 6  
Percent of Initial Sethoxydim Recovered from Surface of  
Corn Leaf After 20°C Growth Chamber Exposure

Tank-mix description	Exposure interval (h)						
	0.25	1	2	3	4	5	7
0.47 l Poast Herbicide alone	82	74	61	50	53	53	44
0.47 l Poast + COC	81	62	36	24	8	10	4
0.47 l Poast + Dash Adjuvant	67	24	8	0	0	0	0
0.71 l Poast Plus Herbicide	62	18	6	2	0	0	0
0.71 l Control <sup>a</sup>	64	53	51	49	31	27	11

<sup>a</sup> Control is 120 g/l sethoxydim with 20 g/l emulsifier in Aromatic 150 solvent. Poast Plus is 120 g/l and Poast is 180 g/l sethoxydim, respectively.

sethoxydim control are included for comparison. The Poast Plus formulation afforded the same enhanced rate of absorption as with a tank mix of Poast and Dash.

After 2 h, oil concentrate still has 36% of the applied sethoxydim at the surface (64% absorption), while Poast Plus has effected absorption of 94% of the herbicide.

#### IV. CONCLUSIONS

- Some adjuvant materials affect the photolability of sensitive herbicides.
- An optimal adjuvant composition can enhance herbicide uptake without affecting the rate of photodecomposition.
- Every adjuvant has an optimal use rate.

Light quality plays a significant role in limiting the efficacy of sethoxydim, and this effect is closely related to the rate of sethoxydim uptake. If a set of grass species (corn, green foxtail [*Setaria viridis* (L.) Beauv.], crabgrass [*Digitaria* spp.], and broadleaf signalgrass [*Brachiaria platyphylla* (Griseb.) Nash]) are collectively rated for the amount of herbicide required to yield some level of control across all species, comparison of treatments becomes somewhat easier. Using an inside/outside posttreatment test, the effect of sunlight



can be expressed in terms of herbicide required for 95% weed control ( $GR_{95}$ ). In the case of sethoxydim without adjuvant, there is nearly a threefold loss in efficacy when exposed to UV light relative to nonexposed plants.

Looking at whole plant efficacy, the outside activity of sethoxydim in the presence of Dash is maintained at levels seen in the absence of UV light. This does not happen with COC. The outside plants exposed to UV require more sethoxydim for the same level of control when treated with oil concentrate rather than Dash Adjuvant.

COC actually increased the photodegradation of sethoxydim in the presence of UV light while having an inadequate effect on uptake. Dash Adjuvant significantly increased the rate of uptake while having a minimal effect on UV photodegradation. Thus, with Dash increasing the rate of foliar uptake while not increasing the rate of photodegradation, there is a dramatic effect on the efficacy of sethoxydim compared to COC.

This approach to investigating the adjuvant requirements for sethoxydim has resulted in the development of a superior adjuvant which meets the needs of the active ingredient and formulation. We believe that all products deserve this consideration of biochemical optimization.

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## Chapter 17

**THE INFLUENCE OF ULTRAVIOLET LIGHT ON THE  
PHYTOTOXICITY OF SETHOXYDIM TANK MIXTURES WITH  
VARIOUS ADJUVANTS**

D. McInnes, K. Neil Harker, Robert E. Blackshaw, and William H. Vanden Born

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## ABSTRACT

Experiments were conducted at three locations in Alberta to evaluate the effect of photodegradation of sethoxydim {2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one}. The degrading effect of ultraviolet radiation (UV, 300 to 400 nm) was investigated under field conditions as measured by the phytotoxic activity of sethoxydim on preselected samples of volunteer barley (*Hordeum vulgare* L.). Physical screening treatments were employed to control the spectral quality of radiant energy impinging on sethoxydim-treated plants. Several spray adjuvants (oil concentrate, ammonium sulfate, BAS 815, BAS 890) were also examined in mixtures with sethoxydim to determine their influence on sethoxydim activity on barley. Visible light (400 to 700 nm) had little or no influence on sethoxydim activity. However, exposure to UV radiation often dramatically reduced the activity of sethoxydim. The inclusion of adjuvants in the spray mixture counteracted some of the deleterious effects of UV radiation. Of the adjuvants tested, BAS 815 or BAS 890 most effectively preserved sethoxydim activity in the presence of UV radiation.

## I. INTRODUCTION

The herbicide sethoxydim controls a broad range of grass weeds in numerous broadleaved crops.<sup>10</sup> The ability of sethoxydim to control both annual and perennial grasses under a wide variety of environmental conditions with excellent crop tolerance has prompted producers of broadleaved crops to make the herbicide a major part of their weed control program. In Canada (1988), approximately 20% of the canola (*Brassica napus* L., *B. campestris* L.) acreage and 80% of the flax (*Linum usitatissimum* L.) acreage that is treated with herbicides is treated with sethoxydim.

Those involved in research with sethoxydim may be aware of some of the interesting characteristics of the herbicide. Adjuvants, particularly oil concentrates and more recently ammonium sulfate,<sup>2,7</sup> significantly improve sethoxydim activity. There are also reports which indicate that sethoxydim is less stable in the presence of heat and light, and that it is rapidly metabolized by plants. Campbell and Penner<sup>1</sup> observed that after 24 h, less than 2% of applied sethoxydim existed in susceptible and tolerant plants. They noted that seven of nine metabolites in the plants cochromatographed with thermal- and phototransformation products of sethoxydim. Several authors have demonstrated photodecomposition of other herbicides in aqueous solutions.<sup>3,4,6,12</sup> In addition, sethoxydim often exhibits superior herbicide activity under greenhouse or other controlled conditions when compared to field conditions. These observations led to the hypothesis that sethoxydim activity in the field may be significantly influenced by solar radiation. Tanaka et al.<sup>11</sup> have noted that only a limited amount of research has been conducted in the area of photodegradation of herbicides, and even less on the specific effects of herbicide additives on photodegradation. This project was undertaken with the following objectives: (1) to determine the effectiveness of several adjuvants with sethoxydim, (2) to determine if UV radiation alone influences sethoxydim activity, and (3) to determine the interaction of UV screening treatments on sethoxydim in the presence and absence of several adjuvants.

## II. MATERIALS AND METHODS

Field experiments were conducted at three locations (Lacombe, 52.30° N 113.42° W; Olds, 51.50° N 114.06° W; and Lethbridge, 49.43° N 112.48° W) in Alberta, Canada in 1988. Barley was cross-seeded in flax to simulate an infestation of volunteer barley. The experiments were designed as split plots with seven herbicide treatments (Table 1) as main

TABLE 1  
Notations of the Herbicide/Adjuvant  
Treatments to be Used in the Tables and  
Figures

Notation	Sethoxydim	Adjuvants
Untr	—	—
Stan	0.25	1% OC <sup>a</sup> + 2.0 AS <sup>b</sup>
- Adj	0.15	—
Oil	0.15	1% OC
O + AS	0.15	1% OC + 2.0 AS
815	0.15	1% BAS 815
890	0.15	1% BAS 890

<sup>a</sup> OC, paraffin-base mineral oil (83%) and surfactant (17%).

<sup>b</sup> AS, BASF liquid ammonium sulfate (490 g/l).

TABLE 2  
Notations of the Screening Treatments to be Used in  
the Tables and Figures

Notation	Screen	Transmission
Open	—	Complete
OP1 (+ UV)	Clear acrylic <sup>a</sup>	Both UV and visible
OP2 (- UV)	Clear acrylic	Only visible
Mirror	Reflective acrylic	Neither

<sup>a</sup> Chemacryl Plastics Ltd., Rexdale, Ontario, Canada.

plots and four UV screening treatments (Table 2) as subplots replicated four times. At the time of treatment, 15 uniform barley plants were ringed in each subplot for subsequent barley harvest. A CO<sub>2</sub>-pressurized sprayer that delivered a water volume of 100 l/ha at 276 pKa was used to apply the herbicide/adjuvant treatments when the barley was in the three- to five-leaf stage with zero to two tillers. All spray treatments were applied at approximately 11:00 a.m. Mountain Standard Time. The UV screening treatments were applied immediately after the spray treatments and were left covering the plots until sunset (approximately 11 h elapsed time). An LI-1800 LI-COR portable spectroradiometer was used to measure the electromagnetic spectrum (from 300 to 850 nm) transmitted through the screening treatments. Three measurements for each 10-nm portion of the spectrum (300 to 850 nm) were recorded, and the average is presented in Figure 1 (transmission values are expressed as the percent of the open [no screen] treatment). The following ratings and parameters were also measured: visual barley control ratings, barley fresh weight, barley head counts, barley plant counts, barley mortality, and flax fresh weight. All the data were subjected to an analysis of variance and means were separated either by Duncan's multiple range test ( $p < 0.05$ ) or by single degree-of-freedom contrasts with their associated probabilities.

### III. RESULTS AND DISCUSSION

#### A. EFFECTIVENESS OF THE PHYSICAL SCREENS

Spectroradiometer measurements confirmed that the UV screening treatments were working according to specifications. The OP1 and OP2 screens transmitted at least 90% of the

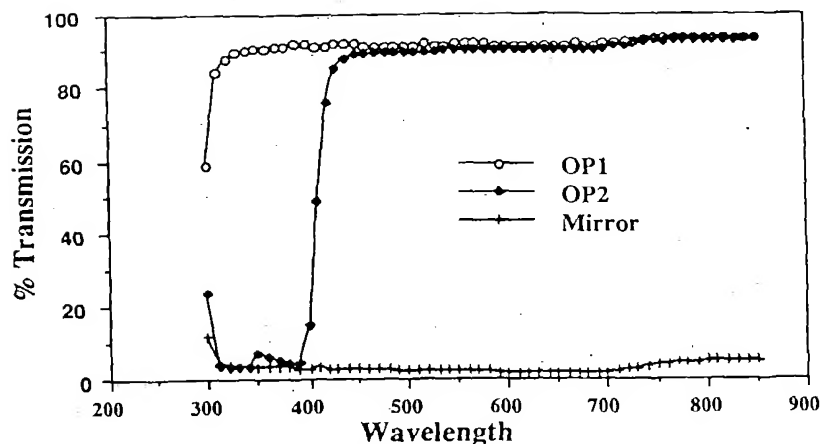


FIGURE 1. Transmission of radiant energy as determined by spectroradiometer readings from 300 to 850 nm; PAR (400 to 700 nm) with no screen =  $1965 \mu\text{E m}^{-2} \text{ s}^{-1}$ . Values are expressed as a percent of the open (no screen) treatment to yield percent transmission.

visible light (400 to 700 nm), and the mirror treatment screened out all direct visible light (Figure 1). The OP2 screen also screened out virtually any UV radiation detected under the open and OP1 screening treatments (300 to 400 nm). Temperature and relative humidity under the different screens did not vary among screening treatments.

#### B. LOCATION ANALYSIS

Only barley fresh weight data will be presented to indicate the various treatment effects; the analysis of other parameters led to similar conclusions. Location by treatment interactions were significant ( $p < 0.01$ ); therefore, locations were analyzed separately and are presented separately. Most data will be presented without averaging over herbicide or screening treatments, since all herbicide treatment by screen interactions were significant ( $p < 0.01$ ).

#### C. OVERALL HERBICIDE ACTIVITY

In general, barley control was good at all locations with most herbicide treatments (Table 3). Most adjuvant treatments with the low rate of sethoxydim (0.15 kg/ha) gave similar barley control to the standard treatment of sethoxydim (0.25 kg/ha with oil concentrate 1% [v/v] and ammonium sulfate [2.0 kg/ha]). Without any adjuvant, sethoxydim at 0.15 kg/ha did not provide adequate barley control.

#### D. VISIBLE LIGHT EFFECTS

Our results clearly indicate that screening out visible light in addition to UV light does not further enhance sethoxydim activity. At Lethbridge, none of the sethoxydim/adjuvant treatments were significantly affected when visible light was screened out in addition to UV radiation (Figure 2). The minus adjuvant treatment had the lowest  $p$ -value for the contrast between the OP2 (-UV) and the Mirror (-UV, -visible) at  $p = 0.38$ ;  $p$ -values for the remaining sethoxydim/adjuvant treatments were all  $\geq 0.84$ . Data from the other two locations confirmed that visible light did not significantly influence sethoxydim activity (data not shown). A major part of the remaining data (Figures 3 to 5) indicate that UV radiation alone can dramatically reduce the phytotoxicity of sethoxydim applications under field conditions. Therefore, UV radiation was much more detrimental to sethoxydim activity than visible light. These results agree with those of Harrison and Wax.<sup>8</sup>



TABLE 3  
Summary of Barley Control with  
Sethoxydim at Three Locations. Means  
are Averaged Over the Four Screening  
Treatments

Treatment	Percent control <sup>a</sup>		
	Lacombe	Olds	Lethbridge
Untr	0 a	0 a	0 a
Stan	85 c	100 c	99 d
- Adj	38 b	68 b	30 b
Oil	74 c	96 c	66 c
O + AS	75 c	100 c	91 d
815	79 c	99 c	100 d
890	78 c	100 c	97 d

Note: Means within a column followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

<sup>a</sup> Percent control =  $100 - [(\text{treatment fresh wt} / \text{untreated fresh wt}) \times 100]$ .

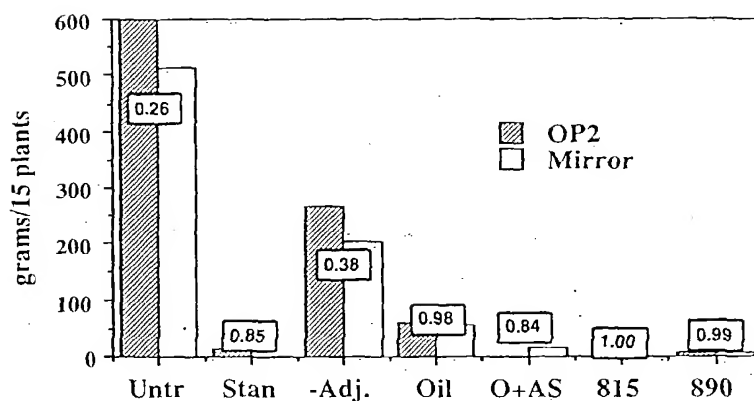


FIGURE 2. The effect of OP2 (-UV) and Mirror (-UV, -visible) screening treatments within individual herbicide/adjutant treatments on barley fresh weight (Lethbridge). Numbers within or above individual herbicide/adjutant treatments on the bargraph are *p*-values for the OP2 vs. Mirror contrast.

#### E. REMOVAL OF UV RADIATION VS. THE ADDITION OF ADJUVANTS

Comparing sethoxydim applied without adjuvants or UV radiation to the same treatment with UV radiation leads to the obvious conclusion that UV radiation has a detrimental effect on sethoxydim activity (Figures 3 to 5). The question then arises: is it possible to retain a high level of sethoxydim activity when adjuvants are applied with sethoxydim in the presence of UV radiation?

Generally, sethoxydim activity was somewhat greater with adjuvants in the presence of UV radiation than if UV radiation was removed and sethoxydim was applied without adjuvants. (That is not to say, as we will discuss below, that adjuvants have value only in overcoming the effects of UV radiation.) At Lacombe and Olds (Figures 3 and 4), the above



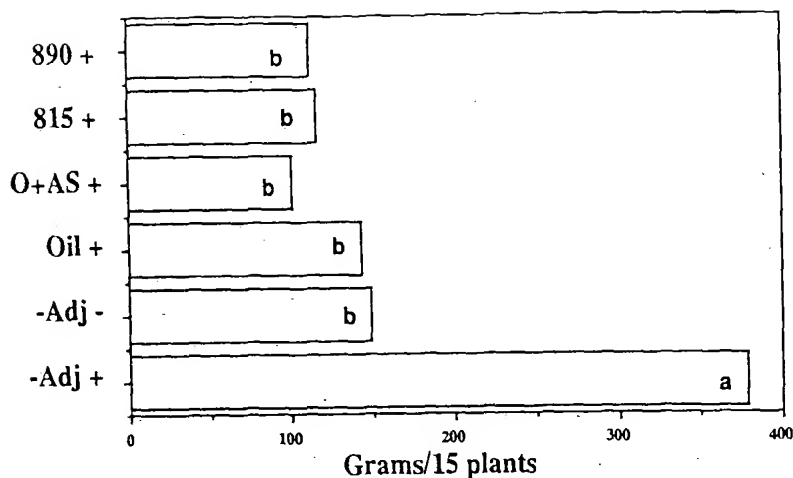


FIGURE 3. The effect of sethoxydim with adjuvants and with UV radiation (OP1; designated as "+" after adjuvant notation) vs. sethoxydim without adjuvants and without UV radiation (OP2; designated as "-" after adjuvant notation) on barley fresh weight (Lacombe). Bargraph portions with the same letter are not significantly different according to Duncan's multiple range test at the 5% level.

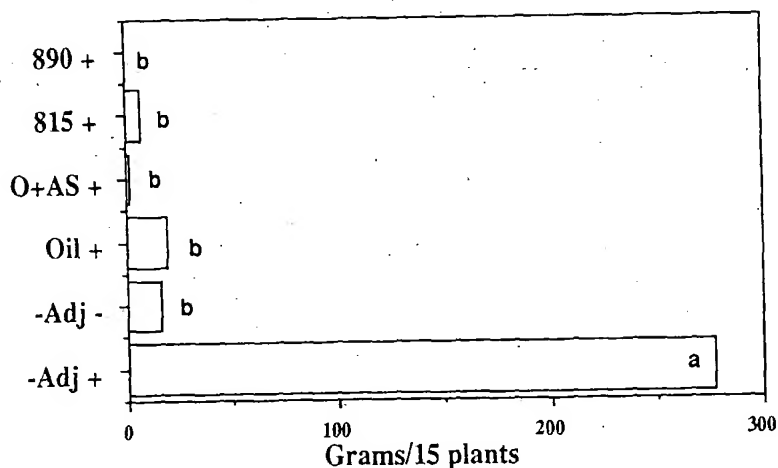


FIGURE 4. The effect of sethoxydim with adjuvants and with UV radiation (OP1; designated as "+" after adjuvant notation) vs. sethoxydim without adjuvants and without UV radiation (OP2; designated as "-" after adjuvant notation) on barley fresh weight (Olds). Bargraph portions with the same letter are not significantly different according to Duncan's multiple range rest at the 5% level.

comparison was not statistically significant, and all adjuvants provided a similar level of sethoxydim activity. However, at Lethbridge (Figure 5), adding BAS 815 or BAS 890 to sethoxydim provided better control than did screening out UV radiation. This suggests that specific adjuvants may add some additional activity to sethoxydim which cannot be accounted for by simply screening out UV radiation.

This study was not designed to determine the individual mechanisms of specific adjuvants. The adjuvants used herein probably increased both the amount and rate of sethoxydim

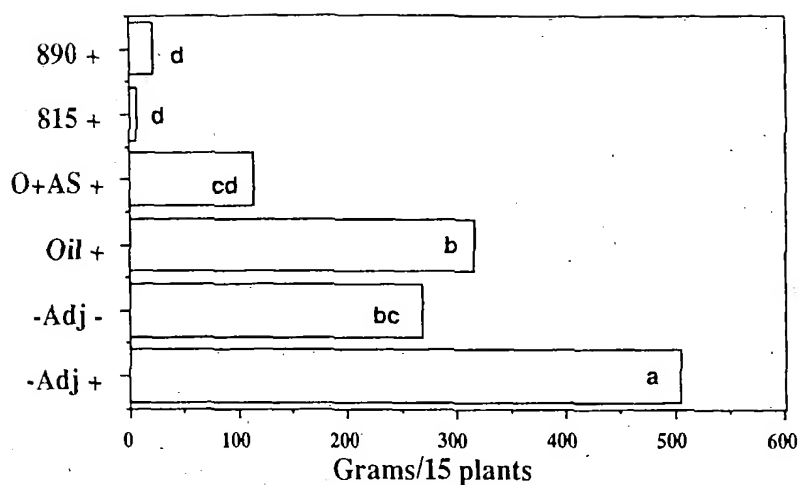


FIGURE 5. The effect of sethoxydim with adjuvants and with UV radiation (OP1; designated as "+" after adjuvant notation) vs. sethoxydim without adjuvants and without UV radiation (OP2; designated as "-" after adjuvant notation) on barley fresh weight (Lethbridge). Bargraph portions with the same letter are not significantly different according to Duncan's multiple range test at the 5% level.

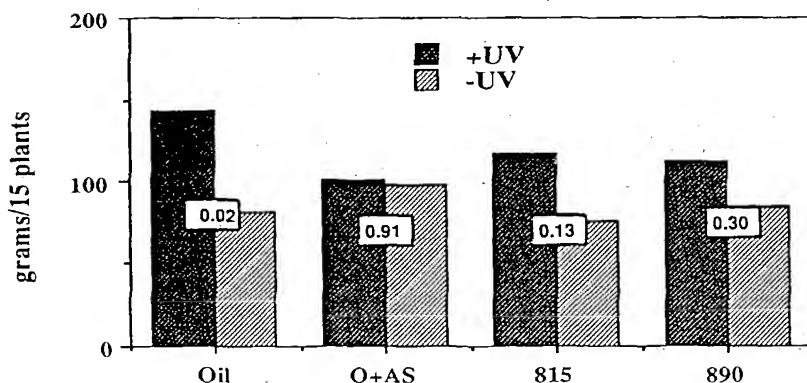


FIGURE 6. The influence of ultraviolet radiation (+UV = OP1, -UV = OP2) on sethoxydim/adjuvant treatments on barley (Lacombe). Numbers within or above individual herbicide/adjuvant treatments on the bargraph are *p*-values for the +UV (OP1) vs. -UV (OP2) contrast.

absorption.<sup>5,9,13</sup> It is obvious that the former mechanism would increase the activity of a sethoxydim treatment. However, in the case of sethoxydim, the latter mechanism could also markedly increase sethoxydim activity by decreasing the time the spray mixture would be directly exposed to UV radiation on leaf surfaces (i.e., UV protection by avoidance).

The least effective adjuvant in the current study was oil concentrate. Specific contrasts within individual adjuvant treatments indicated that the activity of the oil concentrate/sethoxydim treatment could be increased when UV radiation was screened out. In Lacombe (Figure 6) and Lethbridge (Figure 8), the *p*-values of the above contrasts were 0.02 and 0.001, respectively. At Olds (Figure 7), all of the treatments controlled the barley so well that there was little room for enhancement by screening of UV radiation ( $p \geq 0.65$ ). These results suggest that the absorption benefits of oil concentrates may be partially negated by

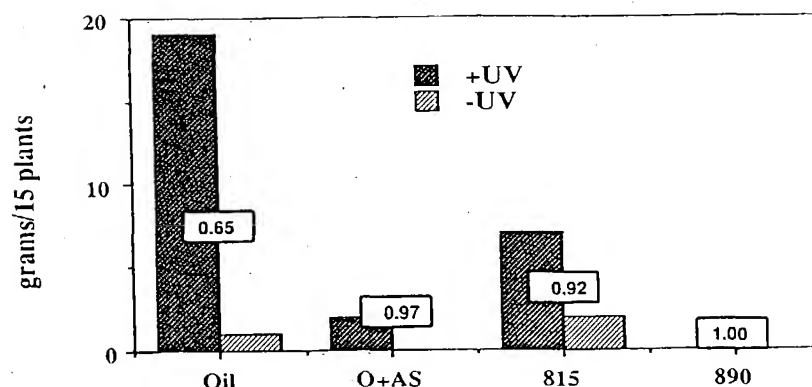


FIGURE 7. The influence of ultraviolet radiation (+UV = OP1, -UV = OP2) on sethoxydim/adjuvant treatments on barley (Olds). Numbers within or above individual herbicide/adjuvant treatments on the bargraph are *p*-values for the +UV (OP1) vs. -UV (OP2) contrast.

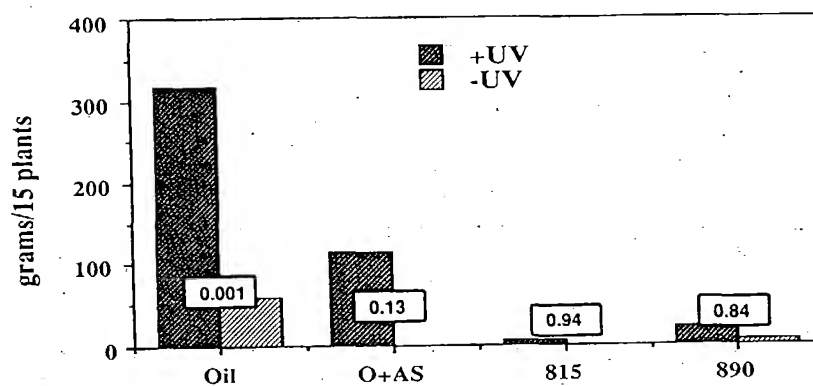


FIGURE 8. The influence of ultraviolet radiation (+UV = OP1, -UV = OP2) on sethoxydim/adjuvant treatments on barley (Lethbridge). Numbers within or above individual herbicide/adjuvant treatments on the bargraph are *p*-values for the +UV (OP1) vs. -UV (OP2) contrast.

the tendency of oil concentrates to increase herbicide photodegradation. Tanaka et al.<sup>12</sup> reported that monuron [*N'*-(4-chlorophenyl)-*N,N*-dimethylurea] photolysis increased in the presence of nonionic surfactants. Harrison and Wax have demonstrated that the photolysis rates of 2,4-D[(2,4-dichlorophenoxy)acetic acid], bentazon [3-(1-methylethyl)-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide], and haloxyfop {2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]-phenoxy]propanoic acid} were increased in the presence of oil concentrates.<sup>8</sup> No significant increases in sethoxydim activity were apparent when UV radiation was screened out of the other adjuvant treatments (Figures 6 to 8). These adjuvant treatments (O + AS, 815, 890) probably effect such rapid sethoxydim penetration that UV radiation effects on sethoxydim are minimal.<sup>5,9,13</sup>

#### IV. CONCLUSIONS

Several conclusions can be drawn from this study.

1. Adjuvants enhance low rates of sethoxydim (0.15 kg/ha) on barley.
2. Screening out UV radiation improves the activity of sethoxydim without adjuvants.

3. With UV radiation screened out, there appears to be no further enhancement of sethoxydim activity when visible light is also screened out (UV degradation vs. photo or visible light degradation).
4. With UV radiation screened out, the activity of sethoxydim alone often parallels that of sethoxydim in the presence of UV radiation with adjuvants (depending on the adjuvant). In the presence of some adjuvants, particularly oil concentrate alone, sethoxydim activity can be increased by screening out UV radiation.
5. With respect to sethoxydim activity, the adjuvants used in this study rank as follows:

$$\text{Oil} < \text{O} + \text{AS} \leq 815 = 890.$$

Further studies are necessary to determine whether the adjuvants in this study facilitated an increased speed and amount of sethoxydim penetration and/or if the adjuvants altered the access or activity of the UV light to the herbicide solution.

### ACKNOWLEDGMENT

We thank Dr. J. Mason Robertson for his critical review of the manuscript.

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## Chapter 18

STABILITY AND ACTIVITY OF CLETHODIM AS INFLUENCED  
BY pH, UV LIGHT, AND ADJUVANT

David C. Bridges, Linford N. Falb, and Albert E. Smith

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## ABSTRACT

Research indicated that abiotic transformation, or degradation, of clethodim {(E,E)-(±)-2-[1-[(3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one} contributes to reduced performance under some environmental conditions. Clethodim was labile in acid aqueous conditions and in UV light. Clethodim loss in UV light was 100, 100, and 99% at pH 5, 6, and 7, respectively. Photodegradation of clethodim was enhanced by the addition of any of five adjuvants. Differences in degradation rate were observed among the adjuvants. Polar degradation products of clethodim were found to be active on sorghum (*Sorghum bicolor* L.) if adjuvant was used. Foliar absorption of <sup>14</sup>C-clethodim and polar degradation products of <sup>14</sup>C-clethodim differed with the five adjuvants. Results indicate that adjuvant selection is a major factor in determining the stability and activity of cyclohexanedione herbicides such as clethodim.

## I. INTRODUCTION

Adjuvants, any material added to a herbicide solution that alters the physical or chemical properties of the solution and which results in modified activity, have been used as an integral part of weed management for many years.<sup>15</sup> Adjuvants have been divided into several classes based on their use and purpose. Among these adjuvant classes are surfactants, emulsifiers, deflocculants, wetting agents, crop oils, and phytobland petroleum or crop oil concentrates. Adjuvants have also been classified as solution modifiers, utility adjuvants, and activators.<sup>8</sup> Activators include surfactants, crop oils, and crop oil concentrates.

The use of crop oils began in the late 1950s and early 1960s to enhance the postemergence activity of atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine].<sup>13,16</sup> More recently, use of crop oil concentrates has increased, especially with the advent of selective postemergence-applied grass herbicides during the early-to-mid 1980s.

Selective postemergence-applied grass herbicides are commonly applied with the addition of various crop oil concentrates at rates of 1 to 2 l/ha. Research has clearly demonstrated differential herbicide efficacy when phenoxy-alkyl or cyclohexanedione-derived herbicides are used with nonionic surfactants, petroleum oil concentrates plus nonionic surfactants, and vegetable oils.<sup>1,9-11,14</sup> These adjuvants are used to improve spray delivery and to increase foliar absorption of herbicides.

Currently, several proprietary products are being marketed. Some are claimed to enhance the performance of grass herbicides. The authors and other researchers<sup>17,18,20,21</sup> have found as little as 17% and generally no more than 40% absorption of sethoxydim {2-[1-ethoxyimino]butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one} applied foliarly in the absence of crop oil concentrate. Therefore, it is not surprising that differential efficacy occurs among adjuvants. Reports indicate that D7, an active ingredient in Dash<sup>®</sup>,\* a commercial, proprietary adjuvant product enhances the foliar uptake of sethoxydim and may render Dash<sup>®</sup> a superior adjuvant compared to crop oil concentrate for use with sethoxydim.<sup>18,24</sup>

Results of field tests indicate that under some environmental conditions, johnsongrass (*Sorghum halepense* L., Pers.) control with sethoxydim and clethodim is greater with Dash than with crop oil concentrate, especially when these herbicides are tank-mixed with bentazon [3-(1-methylethyl)-(1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide)].

Mechanisms responsible for herbicide antagonism have been classed as biochemical, competitive, physiological, and chemical.<sup>12</sup> Chemical antagonisms occur when the antagonist

\* Registered trademark of BASF Corp., 100 Cherry Hill Rd., Parsippany, NJ 07054.



reacts with the herbicide in a way that renders the herbicide less active. Sethoxydim efficacy is reduced in the presence of bentazon presumably by the exchange in  $\text{Na}^+$  ions with the  $\text{H}^+$  from the hydroxyl group of sethoxydim, which yields the Na salt of sethoxydim.<sup>18,19,22,23</sup> Furthermore, Li, K, Cs, Ca, and Mg salts have also been reported to decrease  $^{14}\text{C}$ -sethoxydim absorption,<sup>18</sup> and the addition of calcium hydroxide has been shown to have a mild antagonistic effect on the efficacy of clethodim.<sup>1</sup>

Salt effects have been demonstrated to play an important role in the absorption and efficacy of cyclohexanedione herbicides. Results of some research indicate that solution pH may significantly affect the efficacy of these herbicides. Sethoxydim and clethodim are weak organic acids having  $\text{pK}_a$  values of approximately 4.6. Research has shown that the uptake and biological activity of weak organic acids increases as the pH of the applied solution approaches the  $\text{pK}_a$  of the acid involved. Application of these acid herbicides in relatively acidic solutions restricts the ionization of the acid, which is more lipophilic and penetrates the leaf cuticle more readily than does the corresponding salt(s) of the acid. Chow and MacGregor<sup>4</sup> reported that sethoxydim solutions at pH 4 and 6 were slightly more efficacious than solutions at pH 8, but when ammonium sulfate was added, the pH effect was not observed. Bridges<sup>1</sup> reported little or no pH dependence with sethoxydim or clethodim over a pH range of 3.5 to 7.5. Evans et al.<sup>5</sup> reported that enhanced sethoxydim uptake with Dash® may be partly attributed to the acidic pH of the adjuvant, which retains the herbicide in the protonated form, thus permitting ion trapping.

As previously described, these processes involve the reaction of the herbicide with an antagonist which renders the herbicide less efficacious. Another potential mechanism that would account for reduced herbicide efficacy is abiotic degradation of the herbicidally active component of a spray solution. Sethoxydim has been shown to undergo physical degradation or abiotic transformation,<sup>3,21</sup> with relatively small amounts of the herbicide being absorbed. Therefore, the purpose of our research program over the past 2 years has been to determine if factors other than those previously described control the efficacy of cyclohexanedione herbicides such as clethodim. The objectives were to (1) determine the stability of clethodim under various environmental conditions, (2) identify potential mechanisms of physical degradation, and (3) determine the effect of various adjuvants on the stability of clethodim.

## II. MATERIALS AND METHODS

Four series of experiments were conducted. The first series was conducted to quantify the acid- and/or photocatalyzed degradation of clethodim. The second series was conducted to determine the influence of various adjuvants on the rate of photodegradation of clethodim. The third series of experiments was conducted to determine the relative activity of clethodim and its degradation products. The fourth series of experiments was conducted to measure the influence of various adjuvants on the absorption of clethodim and degradation product(s) into sorghum seedlings.

### A. MECHANISM AND RATE OF DEGRADATION

Experiments were performed with clethodim at 50 ppm in buffered aqueous solutions at pH 5, 6, and 7. They were conducted with both technical-grade (35% active ingredient, a.i.) and commercially formulated clethodim (240 g, a.i./3.8 l) to determine the influence of formulation on stability. The research was initially conducted in the dark to determine the effect of acid catalysis on clethodim degradation. Experiments were also conducted under artificial UV lamps to determine the effect of photocatalysis on clethodim degradation at pH 5, 6, and 7. Clethodim was quantified by high-pressure liquid chromatography (HPLC).<sup>7</sup>

## B. INFLUENCE OF ADJUVANTS

Experiments were conducted to determine the influence of five adjuvants on the photodegradation of technical and formulated clethodim. LI700\* (a mixture of phosphatidylcholine and methylacetic acid); CC-15943 and XE-1167;\*\* Dash® (petroleum hydrocarbons, naphthalene, and oleic acid); and Agrioil®\*\*\* (polyoxyethylene esters) of polyol, fatty acids, and polyoxyalkylene ethers. The treatments were conducted under sunlight and artificial UV lamps. Experimental particulars have been published.<sup>7</sup>

## C. RELATIVE EFFICACY OF CLETHODIM AND POLAR DEGRADATION PRODUCTS

The purpose of this research was to determine the relative efficacy of technical-grade clethodim and polar degradation products of technical clethodim. An aqueous solution of clethodim, pH 5, was exposed to artificial UV light for 4 h, after which the solution was partitioned with acetonitrile. Parent clethodim was assayed by HPLC and fractionated from polar degradation products by liquid partitioning with hexane:water (5:1, v/v). The aqueous solution was partitioned three times and the hexane phase discarded each time. The quantity of clethodim that degraded was calculated by comparing the resulting concentration of parent clethodim to the initial concentration. Mixtures of clethodim and clethodim degradation products were mixed in five proportions — 1:0, 3:1, 1:1, 1:3, and 0:1 — and applied to grain sorghum seedlings for visual efficacy evaluation. Two series of experiments were conducted. One series was initiated at 20:00 h in a greenhouse to permit approximately 10 h of darkness during which maximum plant uptake could occur without further loss from photodegradation. A second series of treatments was initiated at 8:00 h on a clear day.

## D. CLETHODIM ABSORPTION

Experiments were conducted to compare foliar absorption of <sup>14</sup>C-clethodim using each of the five previously mentioned adjuvants. Absorption studies were conducted using ring-labeled <sup>14</sup>C-clethodim and polar degradation products of <sup>14</sup>C-clethodim. Degradation and separation procedures were similar to those previously described. Experimental details have been published.<sup>2</sup>

# III. RESULTS AND DISCUSSION

## A. MECHANISM AND RATE OF CLETHODIM DEGRADATION

Results indicate that clethodim is acid labile and that total clethodim recovery declined over the 20-h period.<sup>7</sup> Clethodim loss was 37, 8, and 0% at pH 5, 6, and 7, respectively (Figure 1), at 20 h in the dark. Furthermore, clethodim was shown to be labile under artificial UV light, with clethodim degradation after 20 h being 100, 100, and 99% at pH 5, 6, and 7, respectively. Degradation rates and products were similar for technical and formulated clethodim.<sup>7</sup> Particulars regarding acid- and photocatalyzed degradation have been published.<sup>7</sup> Separation and identification of degradation products is continuing.

These results indicate that even though the acid or protonated form of clethodim is the preferred species for foliar uptake and absorption, the presence of this species in acid aqueous environments renders it unstable. Furthermore, upon exposure to UV light, the clethodim in these aqueous solutions (emulsions) degraded rapidly. These properties are undesirable, not only because they would limit efficacy once the solution is applied, but also because the lability of acid aqueous solutions will limit, if not preclude, marketing premixes and/or

\* Loveland Industries, Greeley, CO.

\*\* Valent U.S.A. Corp., Walnut Creek, CA.

\*\*\* ChemNut, Inc., Albany, GA.

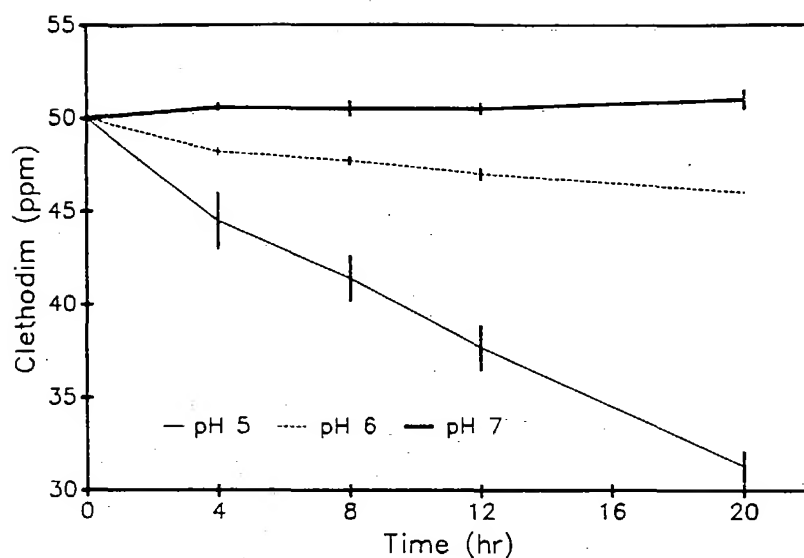


FIGURE 1. Influence of pH on technical clethodim degradation in the dark at 22°C. (From Falb et al., *J. Agric. Food Chem.*, 38, 875, 1990. With permission.)

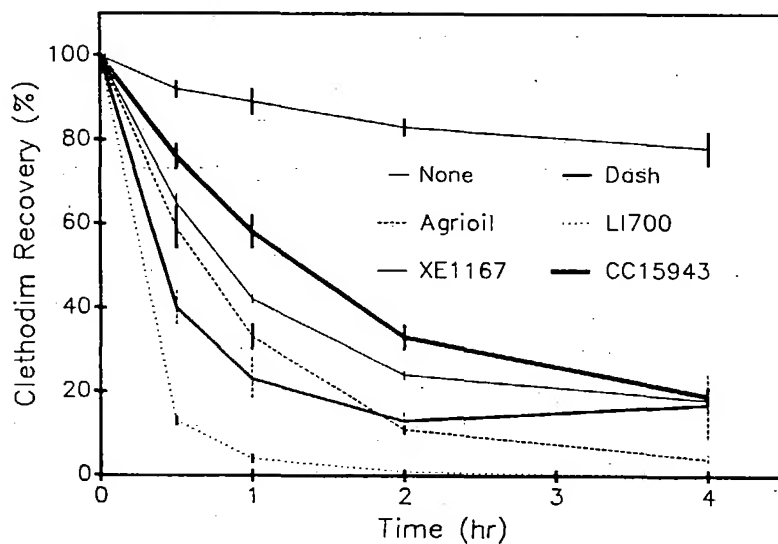


FIGURE 2. Influence of five adjuvants on the degradation rate of 2 EC clethodim in sunlight. (From Falb et al., *J. Agric. Food Chem.*, 38, 875, 1990. With permission.)

ready-to-use formulations of these herbicides. These results may explain why less than half of the herbicide applied actually entered the plant.

## B. INFLUENCE OF ADJUVANTS

All five adjuvants increased the rate of clethodim degradation by two- to sevenfold, compared to the no-adjuvant control (Figure 2). Experiments were conducted in buffered (pH 7) solutions. Since clethodim is relatively stable in the dark at pH 7, the predominant

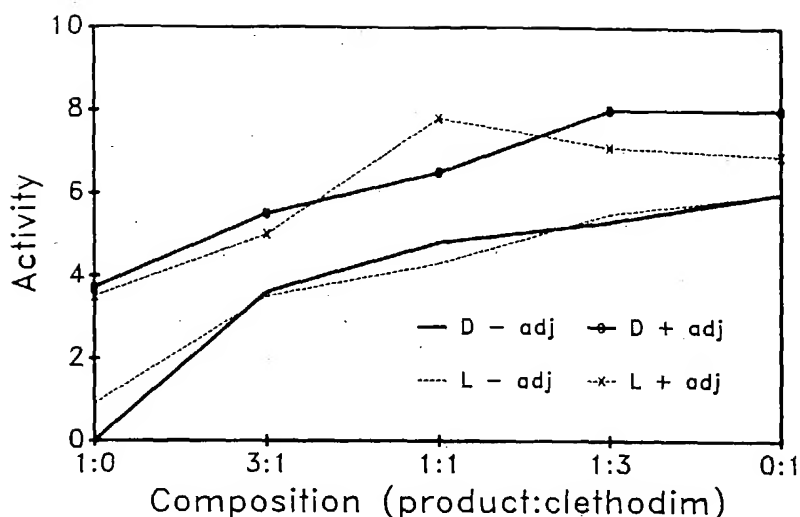


FIGURE 3. Relative activity of clethodim and polar products of clethodim, with and without adjuvant.

degradation mechanism appears to be light dependent. In fact, clethodim degradation in sunlight and under artificial UV light conditions were similar. Half-lives and particulars related to adjuvant effects on clethodim degradation have been published,<sup>6,7</sup> and indicate that degradation rates were in the descending order of: LI700 = Dash > XE1167 = Agrioil > CC15943 > no adjuvant.

Research has clearly demonstrated that the addition of an adjuvant, preferably crop oil concentrate, is required for optimum activity of cyclohexanedione herbicides.<sup>9-11,14</sup> However, our research indicates that the addition of several commonly used adjuvants enhanced photodegradation. The results indicate that macroaggregation of lipophilic clethodim molecules occurs. This could increase the probability of chain reactions, and thus clethodim degradation by free radical mechanisms or energy transfer. Also, since adjuvant addition is required, a prudent approach to adjuvant selection is to select compounds which do not promote degradation processes and which protect the active molecule.

### C. RELATIVE EFFICACY OF CLETHODIM AND POLAR DEGRADATION PRODUCTS

Research results indicate that clethodim was more active than the polar product on sorghum seedlings, particularly in the absence of Dash (Figure 3). The activity of treatments containing clethodim was only about 40% greater when Dash (1%, v/v) was added, compared to no additions of Dash. When only polar product(s) of clethodim were applied, little or no activity was observed in the absence of Dash. However, when Dash (1%, v/v) was added, activity was approximately 75% compared to the application of similar concentrations of clethodim without Dash. Initiating experiments in the greenhouse at 8:00 h vs. 20:00 h had little impact on the activity of clethodim or its polar product(s).

The results show that not only does degradation occur, but that at least some of the degradation products are herbicidally active. They also indicate that because of the polar nature of the products, addition of adjuvant is essential for absorption and subsequent herbicide activity. Therefore, adjuvants capable of mediating the uptake of polar products might enhance the activity of cyclohexanedione herbicides, especially when these herbicides are applied under conditions favorable for degradation of the parent herbicide.

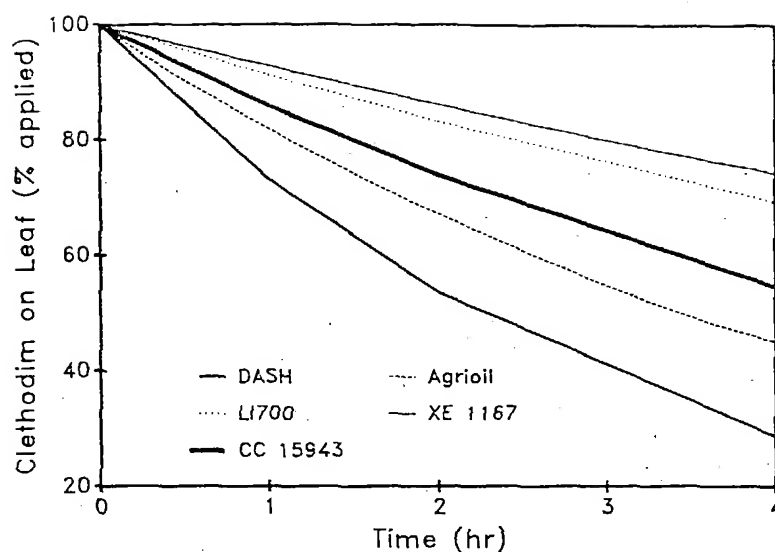


FIGURE 4. Influence of five adjuvants on foliar absorption of  $^{14}\text{C}$ -clethodim.

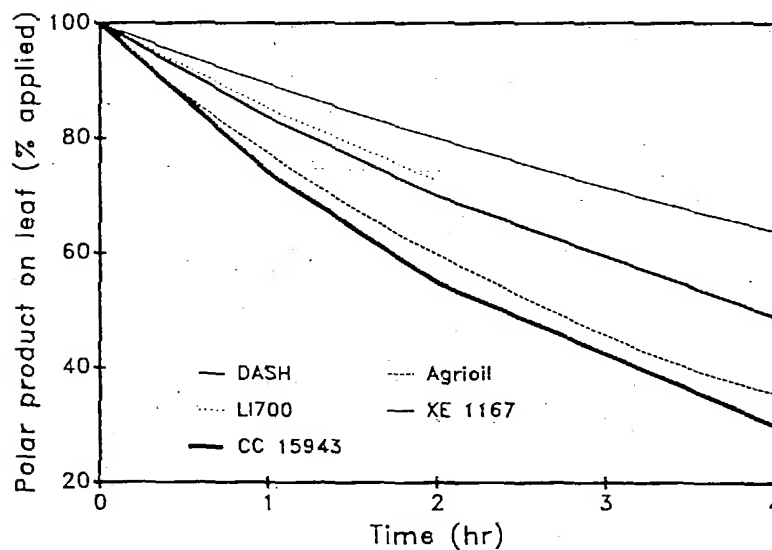


FIGURE 5. Influence of five adjuvants on foliar absorption of polar degradation products of  $^{14}\text{C}$ -clethodim.

#### D. CLETHODIM ABSORPTION

The data indicate that foliar uptake of clethodim was greater (both rate and total amount) with Dash compared to the other adjuvants tested (Figure 4). These data indicate that the uptake of clethodim is more rapid with the addition of Dash than with the other adjuvants, which may contribute to the performance observed with the adjuvant in field tests despite the fact that photodegradation of clethodim in the presence of Dash is more rapid than in the presence of several of the other adjuvants tested, particularly CC 15943.

Foliar uptake of polar degradation products of  $^{14}\text{C}$ -clethodim was greater with Agrioil and CC 15943 than with Dash (Figure 5). In field trials on johnsongrass, clethodim efficacy



with CC 15943 and XE 1167 have been comparable to efficacy with DASH. Even though foliar uptake of clethodim does not appear to have been as rapid with CC 15943, foliar uptake of polar degradation products was more rapid and the photodegradation rate with this adjuvant was less than with Dash.

#### IV. SUMMARY

Results of this research indicate that the lability of clethodim when exposed to acid conditions and/or UV light may significantly affect the efficacy of this herbicide. They also demonstrate that the use of adjuvants with cyclohexanedione herbicides may present effects that are confounded since they appear to be essential for activity, yet often enhance photodegradation. It is apparent that adjuvant selection with these herbicides is a critical decision and may impact the efficacy of herbicide application in ways previously unrecognized. When selecting adjuvants for use with cyclohexanedione herbicides such as clethodim, one should consider compatibility, photodegradation, pH, and absorption characteristics. A prudent approach to adjuvant management with these herbicides would be to select adjuvants which promote herbicide stability and concurrently promote rapid foliar absorption.

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## Chapter 19

**COMPARISON OF THE CYCLIC ETHER-ALCOHOL  
TETRAHYDROFURFURYL ALCOHOL TO OTHER KNOWN  
SOLVENTS**

K. J. Doyel, W. J. McKillip, C. C. Shin, and D. A. Rickard

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## ABSTRACT

Tetrahydrofurfuryl alcohol (THFA 2®-tetrahydrofuryl methanol), as an agrichemical adjuvant that has seen limited commercial applications. THFA's underexploited status is believed due to a lack of publicly available data regarding its characteristics.

Inherently low toxicity, low volatility, biodegradability, and high solvency in both organic and aqueous systems make THFA an attractive candidate for use with agrichemicals. Studies were performed to characterize the chemical with respect to the utility of THFA in agrichemical adjuvant applications.

The results are discussed in comparison to other widely used solvents and carriers. The data presented should provide formulators with another option when selecting formulation chemistry for current or experimental active ingredients.

## I. INTRODUCTION

If one endeavors to create a perfect solvent for use as a coupling agent with various active materials, it would have the characteristics shown in Table 1.<sup>2</sup>

The problem, however, is that few commercial compounds contain all of these attributes. Most commercial adjuvants have been chosen on the basis of cost and availability. Many of these products are well-known solvents and oils. Today, formulators and producers are finding utility in lesser known solvents based on the different cyclic compounds of pyrrole and furan.<sup>3,5</sup>

THFA is a colorless organic solution having the structure shown in Figure 1. THFA is unique in that its structure contains elements of an ether, an alcohol, and a cyclic molecule. THFA is produced commercially by the catalytic hydrogenation of furfural, the furan aldehyde. Furfural is obtained industrially from pentosan containing agricultural byproducts such as corncobs, rice hulls, oat hulls, cottonseed hulls, and sugarcane bagasse.<sup>5</sup>

THFA is unique in that it is easily miscible in water and most organic solvents. In addition, the product has low volatility and can aid in retarding evaporation. Table 2 contains a list of the physical properties of THFA.<sup>5</sup>

Recent findings of new toxicity levels of various solvents have caused some concern with manufacturers and formulators. To combat this, manufacturers are reformulating with different solvents which have lower toxicity characteristics. THFA is one such chemical that is receiving more attention based on its positive toxicity characteristics. Figure 2 compares THFA oral toxicity in rats to oral toxicity levels of other well-known EPA-exempt (40 CFR 180.1001) solvents. The table provides a direct comparison of one parameter, which may be different in other species or conditions.<sup>6,7</sup>

The purpose of this paper is twofold: (1) to introduce the reader to a solvent which has had little or no exposure in the area of agrichemicals and (2) to provide some basic experimental data on the solubility of THFA with well-known agricultural active ingredients.

## II. MATERIALS AND METHODS

The experiment consisted of determining (1) the maximum solubility range of THFA with the chosen active ingredient, (2) the maximum solubility of the THFA/active ingredient mixture in water, and (3) if a 1:100 ratio of mixture to water would result in a stable solution.

Selection of the active ingredients for this experiment was based on the criteria of commercial use, lack of aqueous solubility, and general class of material. Table 3 lists the 52 active materials tested in this experiment. The materials were obtained from Chem Service, Inc., West Chester, PA, and the THFA, from QO Chemicals. All material was of commercial

TABLE 1  
Characteristics of Solvents

Low toxicity  
Low phytotoxicity  
Low volatility  
High flash point  
Ability to solubilize many different active materials  
Coupling ability  
Biodegradability  
Cost effectiveness

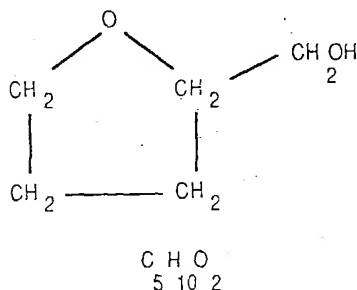


FIGURE 1. Chemical structure of tetrahydrofurfuryl alcohol (THFA).

TABLE 2  
Characteristics of Tetrahydrofurfuryl Alcohol

Boiling point	178°C, 352°F
Freezing point	-80°C, -112°F
Vapor pressure	0.4 mmHg @ 20°C
Density	8.76 lbs/gal
Flash point	165°F TCC method
Soluble in	Water, alcohols, aromatics, esters, ethers, ketones, and chlorinated hydrocarbons
Insoluble in	Coconut, cottonseed, and peanut oils, anthraquinone, dextrose, and paraffinic hydrocarbons
EPA exemption from tolerance as a solvent/cosolvent with no limits per 40CFR 180.1001	
Not phytotoxic in concentrations up to 25%	

purity and was obtained uninhibited in order to eliminate the introduction of other variables to the test. The water for dilution was ordinary tap water provided by the city of Memphis, TN.<sup>1,4</sup>

#### A. THFA/ACTIVE MATERIAL SOLUBILITY

One gram of the selected active material was weighed and placed into a tared 20-ml vial. One gram of THFA was added to produce a 1:1 solution, and the vial was agitated in order to mix the two materials. The solution was visually inspected to determine solubility. If initially the THFA appeared to solubilize the material, the mixture was allowed to stand for 10 min and then reinspected to assure solubility. If the material was not completely solubilized, an additional 2g of THFA was added to produce a 1:1 solution. The same steps were repeated to visually inspect for solubility. The protocol was repeated at concentrations



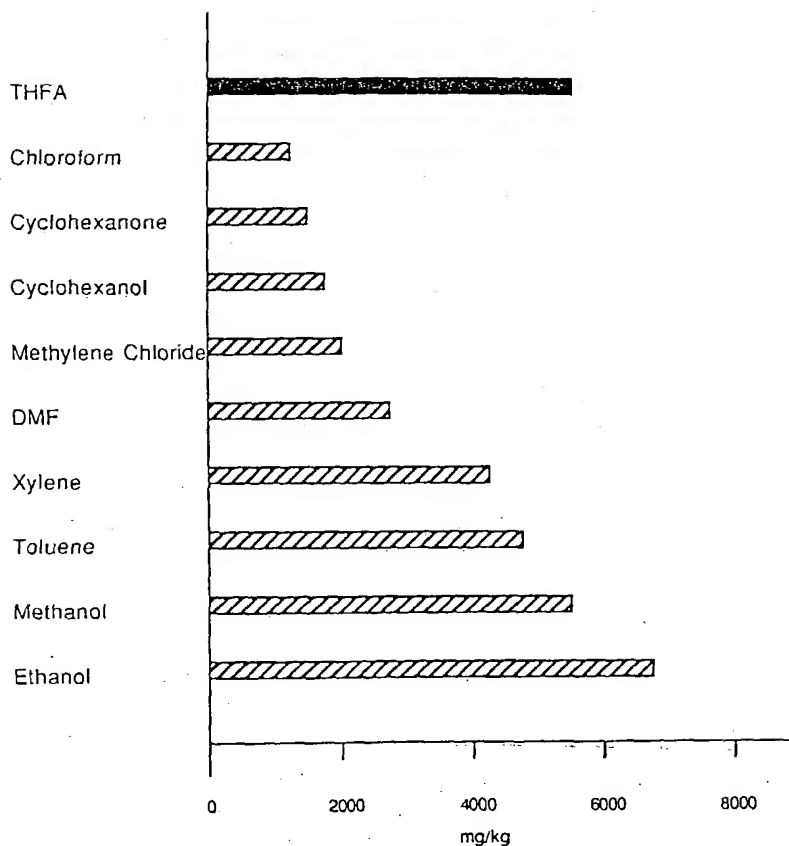


FIGURE 2. Toxicity levels of various solvents (oral toxicity to rats  $LD_{50}$ ).

of 1:9, 1:19, 1:99, and 1:>99 until the material solubilized in the THFA. The temperature was not controlled in the experiment, and was assumed to be 25°C.

#### B. WATER SOLUBILITY IN THFA/ACTIVE MATERIAL MIXTURE

This part of the experiment was designed to measure the coupling ability of the THFA. The solution of maximum solubility in part A was used for this experiment. For mixtures greater than a 1:10 ratio, enough THFA was added to bring the solution to a 10% mixture (11 g total), so as to have enough material for this experiment and part C. For mixtures of 1:19, 1:99, and 1:>99 ratios, 10 g of each solution, as is, were used for this experiment.

The 10 g were placed in a stirred vial. Water was added in increments of 0.25 ml to the mixture. The solution was visually inspected to determine the quantity of water necessary to initiate precipitation of the active ingredient and the volume of water was recorded for each mixture.

#### C. THFA/ACTIVE MIXTURE SOLUBILITY IN 1:100 RATIO WITH WATER

This part of the experiment was designed to determine the coupling ability of THFA in a common commercial dilution ratio (1:100) with water. The mixtures used in part B were also used in this experiment. One gram of the mixture was slowly added with a micropipette to 100 g (or 100 ml) of water. At the first sign of precipitation, the solution was stirred and

TABLE 3  
Materials Used In Test

Class	Material name
Acetamide/anilide	Butachlor Propachlor Propanil MSMA
Arsenicals	Bentazon (Basagran)
Benzothiazole	Carboxin
Carbamate	Carbofuran (Furadan)
Carbamates/thiocarb	Butylate EPTC Molinate Triallate Metolachlor Endosulfan Pendimethalin Diclofop-methyl (Hoelon) PCP (Pentachlorophenol) Chloramben (Amiben) DCPA (Dacthal) Triadimefon (Bayleton) Iprodione (Rovral) Etridiazole (Terrazole) Bromoxynil Maleic hydrazide 2,4-DB MCPA Isofenphos Isazophos (Miral) Naled Phenamiphos Allethrin Norflurazon (Zorial) Diquat Deet MGK-R-11 Benomyl Maneb Zineb Diazinon Dimethoate Disulfoton Fonofos (Dyfonate) Azinphos-methyl (Guthion) Malathion Atrazine Cyanazine Prometon Simazine Propiconazole (Tilt) Bromacil Diuron Fluometuron Terbacil
Chloracetanilide	
Chlorinated HC	
Dinitroaniline	
Diphenyl ether	
Halogenated phenols	
Halogenated acid/derivatives	
Miscellaneous	
Nitrogen compounds	
Phenoxy acids/derivatives	
Phosphate	
Pyrethroid	
Pyridazinone	
Quaternary ammonia	
Repellents	
Thiocarbamates	
Thiophosphates	
Triazines	
Triazole	
Urea derivatives	

TABLE 4  
Solubility (High) of Various Materials in  
Tetrahydrofurfuryl Alcohol (25°C)

1:1 Ratio		1:3 Ratio	
Alfethrin	Isazophos	Azinphos-methyl	MCPA
Butachlor	Isofenphos	Bentazon	PCP
Butylate	MGK-R-11	Bromoxynil	Pendimethalin
Deet	Malathion	Chloramben	Propachlor
Diazinon	Metolachlor	Diclofop-methyl	Propanil
Dimethoate	Molinate	EPTC	Propiconazole
Disulfoton	Naled	Endosulfan	Triadimefon
Etridiazole	Phenamiphos		
Fonofos	Triallate		

Note: Ratio, active to THFA.

TABLE 5  
Solubility (Low) of Various Materials in  
Tetrahydrofurfuryl Alcohol (25°C)

1:9 Ratio	1:19 Ratio	1:99 Ratio	1:>99 Ratio
2,4-DB	Diuron	Atrazine	Benomyl
Bromacil	Iprodione	Carbofuran	DCPA
Carboxin		Fluometuron	Diquat
Cyanazine		Norflurazon	MSMA
Maneb		Prometon	Maleic hydrazide
Terbacil			Simazine
			Zineb

Note: Ratio, active to THFA.

reevaluated. This procedure was repeated until the mixture either went into solution or formed on obvious precipitant.

### III. RESULTS AND DISCUSSION

#### A. THFA/ACTIVE MATERIAL SOLUBILITY

The results of the solubility of various active materials with THFA are shown in Tables 4 and 5. The results show the excellent solubility performance of THFA, with over 60% of the materials tested exhibiting high solubility. In general, phosphates, thiophosphates, carbamates, and acetamides exhibited high solubility with THFA. Thiocarbamates, triazines, and urea derivatives evidenced a lower affinity to dissolve in THFA.

#### B. WATER SOLUBILITY IN THFA/ACTIVE MATERIAL MIXTURE

For our experiment, we chose active materials which have a low solubility in water.<sup>4</sup> From part A, we know that the binary system of THFA and active material will show a high degree of solubility. From a practical standpoint, this can be and has been, used as an acceptable spray mixture for ULV applications. However, a much better mixture may be formed by diluting the binary system with water. Parts B and C of this experiment are attempts to understand and quantify this ternary system.

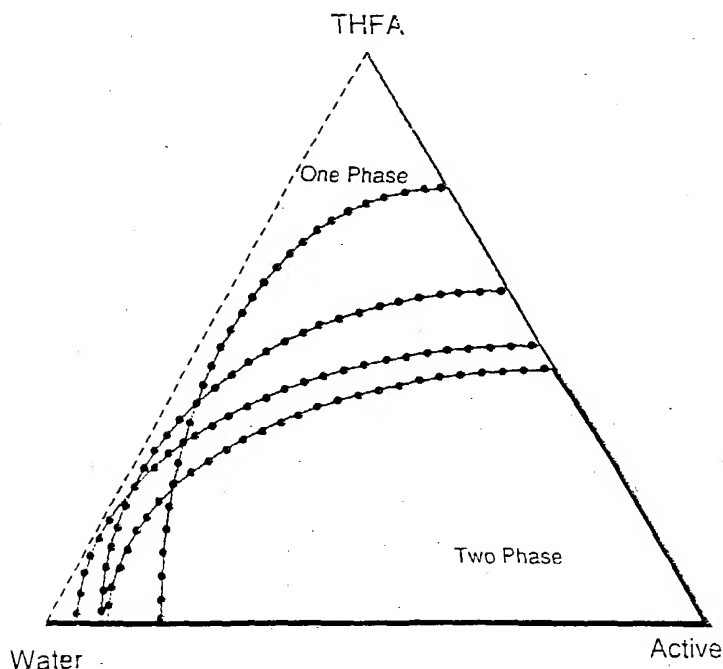


FIGURE 3. Part A — solubility curves of three components.

In order to understand what our experiment is revealing, we must first review what our system looks like by constructing a triangular phase diagram (Figure 3). In this figure, we know that THFA and water are soluble in all portions (denoted by dashes), and that water and active materials are insoluble in portions containing less than 99% water (denoted by thick solid lines). From part A, we determined that blends of THFA and active materials are soluble in varying proportions, depending on the active material chosen (denoted by the thin solid line). The key unknown in this experiment is that we have no information on what shape the solubility curve will take in the interior of the triangle (denoted by the dotted lines).

In Part B of the experiment, we are adding water to the mixture. Figure 4 shows how the addition of water changes the concentration so that the concentration at any point in time will exist somewhat along the tie line drawn in the figure. Saturation of the mixture and precipitation will occur if the tie line intersects the solubility curve. In this experiment, we are testing only one binary concentration of THFA/active material. One could reproduce a portion of this curve by selecting a number of initial starting concentrations and plotting the saturation points on the diagram after the addition of water. Part C of the experiment concerns the area outlined in Figure 5. This area was tested to determine if precipitation would occur in a commonly used dilution ratio (1:100). In addition, it can provide some information about the back side of the solubility curve. A given mixture of the three substances may have a very unique curve that allows two areas of complete solubility (as shown in Figure 4, lower tie line), one at low water concentrations and one at higher water concentrations.

The results of a portion of part B of the experiment are shown in Table 6. These results show that the addition of THFA will couple the active material up to a certain point. THFA

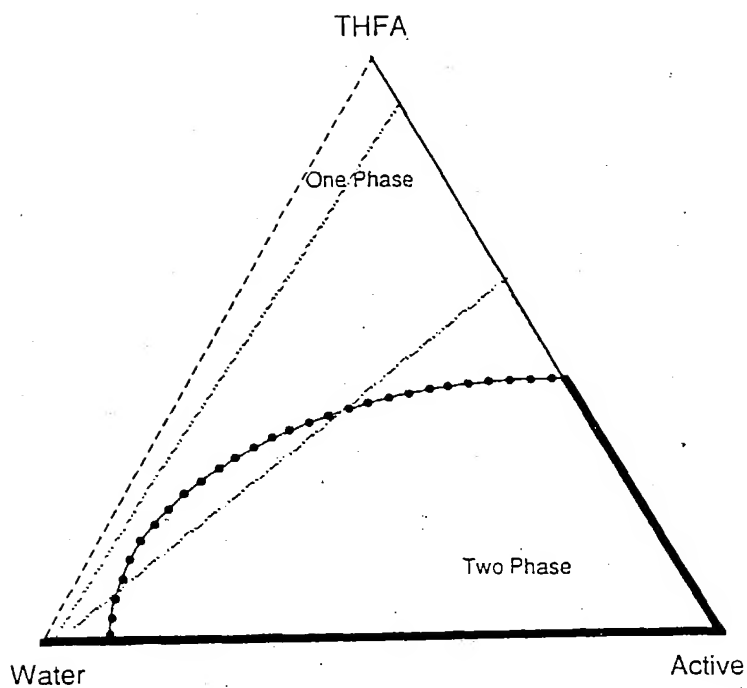


FIGURE 4. Part B — tie lines—water addition to THFA/active mixture.

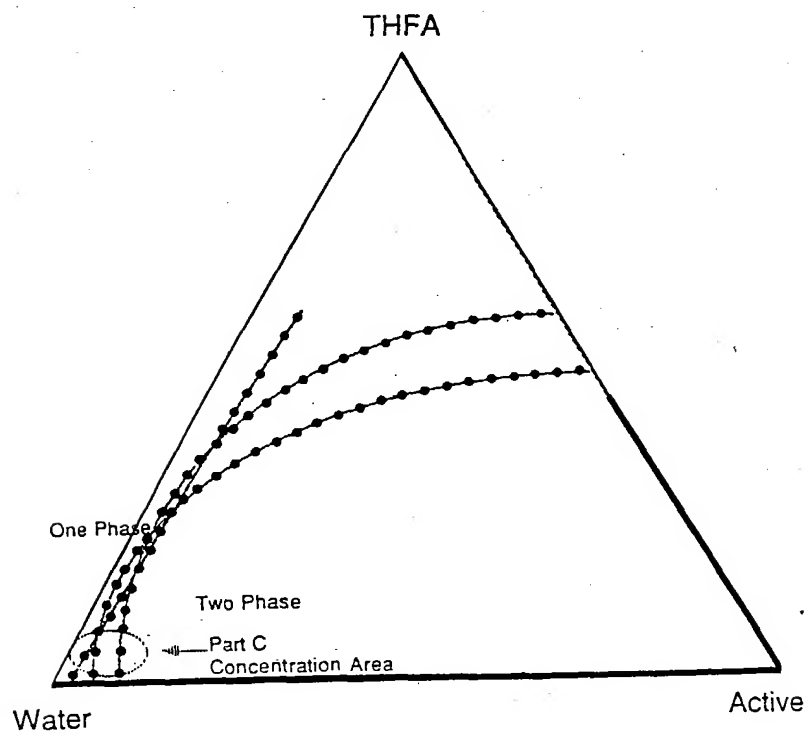


FIGURE 5. Part C — solubility of mixture in 1:100 dilution.



TABLE 6  
Solubility of Water in THFA/Active Mixture

Chemical name	Active solution (%)	Water solubility (water:mixture)
2,4-DB	10	3:10
Atrazine	1	Soluble
Azinphos-methyl	10	7:10
Bentazon	10	Soluble
Bromacil	10	3.25:10
Bromoxynil	10	4.25:10
Butachlor	10	8.25:10
Butylate	10	3:10
Carbofuran	1	6:10
Carboxin	10	8:10
Chloramben	10	Soluble
Cyanazine	10	3:10
DCPA	<1	3.75:10
Deet	10	10:10
Diazinon	10	2.25:10
Diclofop-methyl	10	4:10
Disulfoton	10	4:10
Diuron	5	5:10
EPTC	10	5:10
Endosulfan	10	5:10
Etridiazole	10	5:10
Fluometuron	1	6:10
Fonofos	10	5:10
Iprodione	5	3.75:10
Isazophos	10	6.75:10
Isofenphos	10	5.5:10
MCPA	10	10:10
MGK-R-11	10	3:10
Malathion	10	6.5:10
Metolachlor	10	2.75:10
Molinate	10	6:10
Naled	10	10:10
Norflurazon	1	5.5:10
PCP	10	9:10
Pendimethalin	10	2.5:10
Phenamiphos	10	7.25:10
Prometon	1	5:10
Propachlor	10	4.75:10
Propanil	10	10:10
Propiconazole	10	5:10
Terbacil	10	4:10
Triadimefon	10	9:10
Triallate	10	5:10

appears to do well in having some coupling effect on the broad range of substances tested. An interesting experiment beyond the scope of this study would be to continue the addition of water to determine if, and at what concentration, the material would resolubilize, and whether this new concentration would be optimal for commercial applications.

#### C. THFA/ACTIVE MIXTURE SOLUBILITY IN 1:100 RATIO IN WATER

As discussed, a point was picked to determine whether THFA would couple the active ingredient in a large dilution of water. Table 7 shows a compilation of the materials that

TABLE 7  
THFA/Active Mixture Solubility in 1:100 Ratio  
with Water

Chemical	Mix concentration active:THFA	Water solubility of active
Soluble		
Allethrin	1:10	Insoluble
Atrazine	1:99	33 ppm
Bromacil	1:10	815 ppm
Carbofuran	1:99	700 ppm
Deet	1:10	Insoluble
Diuron	1:19	42 ppm
Fluometuron	1:99	90 ppm
Naled	1:10	Insoluble
Prometon	1:99	620 ppm
Partially soluble		
Benomyl	1:>99	Insoluble
Bentazon	1:10	Insoluble
Chloramben	1:10	700 ppm

were solubilized. THFA appears to be somewhat effective in getting some of the materials to solubilize in water. As previously discussed, it would be interesting to generate solubility curves for the materials in order to determine an optimal concentration for commercial use.

#### IV. CONCLUSIONS

The results of this study show that:

1. THFA has some unique characteristics which may be of interest to the manufacturer or formulator.
2. THFA alone has good solubility performance with many common active materials.
3. THFA can couple these materials into water; however, three-component equilibrium solubility diagrams should be constructed to determine optimal concentrations for commercial use.

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## *Section II*

Regulation and Importance; Environmental Effects; Spray Deposition and  
Dissipation; Soil Adjuvants; Organosilicone Surfactants, Oils, and  
Emulsifiers

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## REGULATION OF PESTICIDES AND INERT INGREDIENTS IN PESTICIDE PRODUCTS

Edwin F. Tinsworth

The Environmental Protection Agency (EPA) regulates pesticides under two statutes: the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Federal Food, Drug and Cosmetic Act (FFDCA). Recent amendments to FIFRA, proposed amendments to FFDCA and continuing debate in Congress regarding food safety make discussions of registration, reregistration, and special review as they relate to both active and inert ingredients in agricultural chemicals timely. The following is a summary of the EPA's authority to regulate pesticides and adjuvants; the three programs — registration, reregistration, and special review — that are the backbone of pesticide programs at the EPA; and what the future may hold in terms of these processes.

FIFRA requires that all pesticide products sold or distributed in commerce be registered by the EPA. It further requires that the EPA determine that the product, when used according to directions, will not pose unreasonable risk to human health or the environment, taking into account the risks and benefits of the chemical's use. In addition, FIFRA requires the EPA to reregister existing pesticides.

Under the FFDCA, the EPA is authorized to establish tolerances of pesticide residues on raw agricultural commodities (RACs) and food additive regulations for pesticide residues in processed foods.

Prior to the establishment of the EPA, the Food and Drug Administration (FDA) was responsible for establishing tolerances and food additive regulations. In 1961, the FDA published a notice that each component of a registered pesticide product, including inert ingredients, was a pesticide chemical and subject to the requirements of tolerances under the FFDCA. In 1969, they established a policy requiring that certain minimal toxicity data be provided on inert ingredients and stating that the need for data depicting the residues of the inert ingredients in or on RACs and processed food would be dependent on the substance's toxicity. The FDA policy also provided for a less formal clearance process of inerts that were deemed to be generally recognized as safe (GRAS).

The definition established by the FDA clearly indicates that the EPA may set tolerances and food additive regulations for inert ingredients in pesticides. Further, regulations under FIFRA which set forth the data generally required to assess a pesticide's risk also state that the EPA can require data on inert ingredients in pesticide products. Additionally, the EPA's authority to require data extends to end use-formulated products plus any recommended vehicles and adjuvants not part of the product, but mixed with the product at the time of its use.

Despite the fact that the EPA can regulate adjuvants under existing and past authority, little testing has been required to date. About 50% of the approximately 1200 existing inert ingredients used in pesticide products have been cleared for use under the FFDCA. Over 100 of these have been deemed GRAS by the FDA in the past. Until recently, most regulatory actions and data requirements under FIFRA for food-use and non-food-use pesticides have focused on the potential risks posed by the pesticide active ingredients in formulated products. The basic exception is that the EPA requires product chemistry and acute toxicity testing on the formulated, or end-use product, thereby characterizing the acute risks of the combination of active and inert ingredients that make up that product.

When the EPA registers a pesticide, the burden of proof that the pesticide will not result in unreasonable adverse effects lies with the prospective registrant of the pesticide. In order to prove that the pesticide meets this statutory standard, data must be developed to characterize acute, subchronic, and chronic toxicity, reproductive effects, oncogenicity, teratogenicity, metabolism, and mutagenicity. Product chemistry data showing the chemical's fate in the environment, data regarding potential ecological effects, and residue chemistry data are also required to support registration. In most cases, these data are required to be conducted on the active ingredients contained in the product. Prior to registration of the formulated product, acute toxicity and product chemistry data must also be submitted for the product as formulated. As part of the information submitted to support registration, the prospective registrant must disclose to the EPA all ingredients in the pesticide, including inert ingredients, and the percentages at which they will occur in the product. Until 1987, however, the EPA focused little attention on that percentage of the product comprised of inert ingredients.

In addition to registering pesticides, the EPA was directed by amendments to FIFRA in 1972 to reregister existing pesticides, some of which were registered as long ago as 1947. Approximately 40,000 products containing one or more of over 800 active ingredients were to be reviewed to determine whether the existing database was adequate to support registration by current standards. To accomplish this objective, the EPA developed the registration standards process. That process begins with a review of the existing database for a given active ingredient, and results in a determination of the validity of the existing data, identification of gaps in the database, whether tolerances are set appropriately, and preliminary determinations of risk if these can be ascertained from the existing data. Based on the available data, the EPA develops a regulatory position regarding the continued registration of the chemical. The EPA's position can include requirements to modify labeling or manufacturing processes, restrict the chemical to use by certified pesticide applicators, or recommend the chemical for a special review. The registration standard document, in which the EPA's position on the chemical and its rationale for that position are discussed, also identifies and requires development of any data necessary to make a final regulatory decision on the chemical.

For many of these old chemicals, studies considered critical by today's standards are missing. Other studies, conducted according to good scientific practices at the time, are outdated by today's standards. Once these new data are received, the EPA undertakes a second review of the chemical to determine whether unreasonable adverse effects may result from its use. If the new data indicate that the risk may be unreasonable, an in-depth study of the risks and benefits associated with its use will be conducted.

This process — the special review process — is a full and public risk/benefit analysis. The result of the special review can be a determination that some or all uses of the chemical be cancelled, that the registration continue in effect without modifications, or that the registration continue in effect with certain modifications. These modifications may be to any aspect of the pesticide registration, such as changes in protective clothing requirements, reentry and preharvest intervals, modifications to the manufacturing process or type of formulation, or changes in application rates, frequency, or methods of application.

In certain cases, each process — registration, reregistration, and special review — may involve a requirement that some data be developed on the end-use, formulated product. However, these processes generally focus on the risks posed by the active ingredients in pesticides.

Recognizing that, while pesticidally inert, some adjuvants may be of toxicological or environmental concern, the EPA developed in 1987 a policy to begin addressing potential risks from inert ingredients in pesticide products. In summary, the policy and procedures



were developed to reduce the potential adverse effects from use of toxic inert ingredients, and to amass sufficient data to evaluate inert ingredients to determine whether they are of toxicological significance or should be permitted to be incorporated into pesticide formulations without further regulatory action.

To work toward these objectives, the EPA first placed each of the 1200 existing inert ingredients in pesticide formulations into one of four categories. The inerts on list 1 are those of known toxicological concern. Inert ingredients on List 2 are potentially toxic and are high priority for testing. List 3 inerts are those of unknown toxicity, and an inert ingredient is identified on List 4 if there is evidence that it will pose minimal, if any, risk to human health or the environment.

On List 1, the EPA identified over 50 inert ingredients of toxicological concern. In determining which ingredients should be identified on List 1, the EPA considered evidence of potential carcinogenicity, adverse reproductive effects, neurotoxicity, other chronic effects, and developmental toxicity. If these effects were demonstrated in laboratory or human studies and the data had been peer reviewed and found valid, the EPA placed this inert on List 1. In addition, if documented ecological effects existed or if the ingredient had the potential to bioaccumulate, the ingredient was assigned to List 1.

On List 2, the EPA identified over 60 ingredients. These ingredients are potentially toxic and are high priority for further testing to better characterize the potential effects from exposure. Ingredients were placed on List 2 if they were structurally similar to chemicals known to be toxic or if existing data suggested a basis for concern. Most of the adjuvants on List 2 have been designated for further testing through the National Toxicology Program, the EPA's Office of Toxic Substances, or other regulatory or government bodies.

List 3 contains inert ingredients used in pesticide products about which not enough is known to imply toxicological significance or safety. There are approximately 800 adjuvants on List 3.

Finally, List 4 contains the names of ingredients that are known to be of minimal concern. Included on this list are those substances that the FDA has deemed GRAS. There are approximately 300 inerts on List 4. The EPA's policy to ensure that inert ingredients in pesticides do not pose unreasonable risk focuses on those ingredients on Lists 1 and 2. List 1 inerts are being addressed through a multistep approach.

First, registrants of pesticide products that contained substances in this category were encouraged to reformulate their products to substitute an inert ingredient that was not on List 1. As an immediate step to inform pesticide users of the presence of an inert ingredient of toxicological concern, registrants who maintained a List 1 inert in their product were also instructed to amend their product's label to include prominently a statement that "This product contains the toxic inert ingredient (name of inert)". Pesticide products that continued to be formulated with a List 1 inert were not permitted to be released for shipment into the market place after October 20, 1988, unless the label of the product contained the required identification of the toxic inert.

Next, registrants maintaining a List 1 inert in their products would be subject to specific data requirements based on the existing database and the product's use patterns. Because of the demonstrated biological activity of List 1 inerts, the extent of the data required was in some cases as complete as that required to register or reregister a pesticide active ingredient. In some cases, the toxicity database was inadequate and in other cases, the toxicity database of the inert ingredient was complete, but exposure, environmental fate, or ecological effects data were still needed to assess potential risks.

The EPA's 1987 policy announced that in cases where the presence of an inert ingredient in pesticide products appeared to result in unreasonable adverse effects, the EPA might hold a hearing to determine whether the benefits created by inclusion of the specific inert out-

weighed the risks. If the hearing demonstrated that the risks outweighed the benefits, the EPA would take steps to cancel products containing the inert unless those products were reformulated with an inert not identified on List 1. While abbreviated, this provision of the EPA's policy provides a mechanism similar to the special review process to address unreasonable adverse effects resulting from the use of an adjuvant in pesticide products.

Finally, if the EPA determined that an ingredient on List 1 was actually pesticidally active, it would proceed to reclassify the ingredient as active. In these cases, products containing the ingredient would have to be relabeled to identify the ingredient as active and the ingredient would be subject to the full range of testing necessary for pesticide active ingredients.

For adjuvants on List 2, potentially toxic and high priority for testing, the EPA is tracking the development of data under its own and other government or private organizations. As data are developed, these ingredients will be evaluated to determine whether it is appropriate to place them on List 1 (those of toxicological significance) or on List 4 (those of minimal concern). If placed on List 1 after a review of data, these adjuvants will be subject to the same procedures being applied to ingredients currently assigned to List 1.

Since the EPA has to set priorities for its resources, no specific actions on List 3 ingredients are planned at the present time. However, if more is learned regarding an ingredient on List 3, the EPA may determine that it should be placed on List 1, 2, or 4.

As large a task as beginning to regulate a subset of adjuvants is, it is made even larger through the introduction of new pesticides containing existing toxic adjuvants, or containing new adjuvants. To curb increased use of existing toxic or potentially toxic inerts, and to preclude the list of these adjuvants from growing even longer, the EPA is addressing new uses of existing inert ingredients and new inert ingredients in pesticide products as they are identified. While the EPA does not "register" inert ingredients, the requirements set out by it for approval of inert ingredients parallel those for registering a pesticide.

New products that contain a List 1 inert will not be registered unless the product is closely similar in composition and use to an existing product. If that is the case, the product will be conditionally registered subject to the data requirements imposed on other registrants of products containing the specific inert. Until those data requirements are satisfied, the product will have on its label an identification of the specific adjuvant as being of toxicological significance.

Prior to registration of any products that contain a new inert ingredient — an adjuvant not on any of Lists 1, 2, 3, or 4 — a minimum set of data are required. These data, a subset of those required to support registration of a pesticide, include residue chemistry, product chemistry, a 90-d feeding study in rodents and dogs, a subchronic dermal study, a teratology study in rodents, and data to determine whether exposure to the ingredient may result in gene mutation, structural chromosome aberration, or other genotoxic effects. In addition, acute studies to determine toxicity to fish, invertebrates, and avian species are required along with hydrolysis, aerobic soil metabolism, photodegradation in water and soil studies, and an octanol-water partition coefficient study. If this subset of data demonstrates that the adjuvant may pose unreasonable risk to human health or the environment, additional data up to the full range generally required for registration of a pesticide may be imposed.

Since issuance of its policy in 1987, the EPA has reviewed the available data base for each List 1 inert ingredient and has called in data from the registrants of products that continue to contain these toxic inerts. From the data requirements already issued to registrants of over 700 products, registrants of only a very few products have committed to supply the necessary data. Most products have been reformulated or the registrant has, in response to the data requirements, committed to reformulate to remove the List 1 adjuvant. In addition, some pesticide registrations are being suspended for registrants' failure to respond to the notice describing the data requirements.

Two inerts that had been identified on other lists will soon be proposed for inclusion on List I. When this action is completed, these substances will be subject to the procedures for existing List I inert ingredients. Reviewing the actions that have taken place since the EPA instituted its inerts policy, the EPA believes that it is succeeding in ensuring that unreasonable risk does not result from adjuvants in pesticide products.

In December 1988, the President signed into law amendments to FIFRA. Some people dubbed these amendments "FIFRA Lite" because some of the provisions in the initial bills were not included in the final legislation. However, the EPA prefers to call the amendments FIFRA '88 since they are by no means light and significantly affect both the EPA and the pesticide industry.

The new provisions direct the EPA to develop regulations to govern the transport, storage, and disposal of pesticides, to expedite certain types of registration requests while at the same time reducing the backlog of registration requests currently in-house, and give the EPA authority to collect fees from registrants for registering a pesticide and for maintaining that registration. These fees are intended to assist the EPA in meeting the goals of expedited registration and of the new reregistration process set forth in the amendments.

The reregistration provisions of FIFRA '88 are some of the most significant in terms of resulting in changes to established processes within the Office of Pesticide Programs. The amendments set forth specific procedures and time frames for the EPA to accomplish reregistration and place significant responsibilities on registrants to identify and supply missing or inadequate data to support continued registration. The schedule set forth in FIFRA '88 would allow the EPA to accomplish the review and reregistration of existing pesticides within 9 years — a task the EPA had projected, prior to the amendments, to be completed in the year 2010.

While no provisions were added to FIFRA '88 which specifically address the regulation of inert ingredients, the amendments may yet play a significant role in this regard due to a bill that is being proposed to amend the FFDCA.

The U.S. House of Representatives is currently considering a bill that focuses heavily on the regulation of inert ingredients in pesticide products that are used on food or feed. The proposed legislation, HR 1725, called the Food Safety Amendments of 1989, would substantially rewrite those provisions of the FFDCA that address pesticides.

Historically, the EPA's primary concern with the FFDCA had been a clause of Section 409, which deals with food additive regulations for residues in processed foods. That provision, called the Delaney clause, appears to bar the EPA from considering benefits in determinations of unreasonable risk, as is required under FIFRA. Thus, the Delaney clause poses a continuing contradiction within the regulatory system.

More recently, the EPA has had to address widespread public concern about the overall safety of the American food supply. The Food Safety Amendments, as they are drafted, propose a health-based standard and could assist in dealing with public fears about food safety. That health-based standard is proposed to be used consistently for both raw agricultural commodities and for processed foods, thereby eliminating existing differences in standards for the two groups.

The bill also requires that the EPA reassess existing tolerances, exemptions from tolerances, and analytical methods used to enforce them as well as to reassess determinations that certain substances are GRAS. Further, the bill provides authority to set tolerances for cancelled pesticides that may result in residues on food due to their environmental persistence, and would give the EPA explicit authority to set expiration dates for a tolerance or exemption from the requirement of a tolerance.

While there are many positive provisions in the proposed amendments, there are also some provisions that are of concern to the EPA. The bill does provide for consistent regulation

of residues in both RACs and processed foods by applying a consistent health-based standard to both groups. However, the bill also proposes that benefits not be considered in establishing or maintaining tolerances for pesticides on RACs or food additive regulations for pesticides in processed foods.

FIFRA '88 directs the EPA to complete the reregistration of existing pesticides within approximately 9 years. Under the Food Safety Amendments, the EPA would be required to conduct what amounts to a reregistration of all food-use pesticides in a much shorter time period.

Some of the major difficulties with the bill are those provisions addressing the regulation of inert ingredients in pesticides. If the bill is passed into law as drafted, there will be a significant new burden on the regulated industry and the EPA. Under the bill, only three types of inert ingredients would be allowed for food use:

1. GRAS inerts
2. Those that are essential for the working of a particular active ingredient
3. Those for which it is not scientifically feasible to replace with GRAS substances

Any adjuvant in these latter two groups that remains in a pesticide used on food or feed would require a tolerance for residues on each food to which the inert is applied. Most inert ingredients do not have a database adequate to support tolerances as directed by the bill and they are not normally subject to registration requirements under FIFRA. Generation of the required data is not likely to be economically feasible for many pesticide registrants and may not be economically worthwhile for the producer of the inert ingredient whose total sales for inclusion in pesticides may be small.

If pesticide registrants were to jointly develop data to support only the most useful adjuvants, the resource implications would still be significant. Hundreds of new toxicity studies and thousands of residue chemistry studies would be needed to set tolerances for these chemicals on food and feed crops. With only a limited number of inerts available, pesticide manufacturers may be forced to reformulate their products to exclude inerts that are no longer legal. The EPA will have to review not only the data associated with potentially thousands of tolerance petitions, but will also have to review requests for amended registrations reflecting new formulations. These reviews would need to take place in a timely manner while the EPA is attempting to meet the mandate of FIFRA '88 to expedite certain registration actions and at the same time reduce the EPA's backlog of actions. Under IFRA '88, the EPA is to make reregistration decisions regarding product registrations within approximately 9 years.

While the EPA does not now require a full range of data for inert ingredients, passage of this bill may force the EPA to require all the data necessary to set tolerances prior to making reregistration decisions; thus, registrants would have to conduct and submit data for both the active and inert ingredients in their products within relatively short time frames.

The EPA believes that while it is reasonable to require very stringent health standards for pesticide active ingredients which are designed as poison, adjuvants do not generally pose high risks and less stringent standards are appropriate in many cases. The new food safety bill should recognize the differences between inert and active ingredients in pesticide products and should set appropriate standards and priorities for dealing with each. While we are striving for reasonable regulation of inert ingredients, we do not intend to ignore the fact that some inert ingredients have the potential to result in human or environmental effects of concern.

The foregoing discussion has summarized the current and projected state of pesticide regulation and how the regulation of inert ingredients in pesticides is rapidly catching up to



the regulation of active ingredients. To recap, the EPA initially focused on the potential effects of active ingredients, focusing little attention on inerts. With regulation of actives pretty well in hand, the EPA began to focus more attention on inert ingredients in pesticides. Now, due in part to increased public and federal awareness, Congress is debating more stringent regulation of inerts in pesticides.

Increased attention has been given to the safety of the American food supply and the health of our environment in recent years. The level of knowledge and awareness on the part of the general public, the regulated industry, and the federal government has increased. This increased knowledge and understanding, however, inevitably will result in more questions than were answered by that knowledge. As a result, it is expected that the focus on the health of our people and our environment will continue to grow in coming years.



## Chapter 21

## REGULATORY ISSUES AND ADJUVANTS

John F. McCarthy

The term "adjuvants", which are substances that are intentionally added to pesticide formulations, is preferred to the word "inerts". It is unfortunate that the term "inert ingredients" was used for anything that was intentionally added to a pesticide formulation that has gone through the processes of regulation, legislation, etc. These substances allow not only the delivery of the product, i.e., total delivery and all of the things encumbent in that word, but they maximize performance. Good adjuvants make ordinary chemicals do extraordinary things. They bring out the best. There is a notion that adjuvants or inerts are added to a product as fillers, substances which have no beneficial function. They are perceived as just another way to dupe the consumer, according to self-appointed critics of our industry. This "snake oil" image is augmented by the fact that we do not claim them on our labels. Secrecy creates suspicion, plus there is a terminology issue. Some five different definitions for wetting agents and three or more different definitions of a surfactant do not help. For these reasons, we at the National Agricultural Chemicals Association (NACA) are pleased that this conference is taking place. We are at a critical juncture in the use of pesticides. This conference can help bring balance and science back to a situation which has gotten a little out of hand. The signals are clear — use less pesticides! Adjuvants will play a more critical role than ever in pursuing that strategy. We cannot rely entirely on new chemistry.

Turning now to the regulatory situation, it is fitting and proper that we take a harder look at the adjuvants/inerts situation. It comes as no surprise that some adjuvants have toxicological properties. We seem to forget that everything is toxic, depending on the amount. The fact that a substance causes something to happen in animals is only the first step in the process of risk assessment. The issue is, "What is the probability that the observed effects will happen under the conditions of use and exposure?" We must keep this basic scientific principle in mind as we analyze the risk, and balance that against the benefits, assuming that Congress will continue to allow us to do that.

Now, let us look at some of the current issues. E. Tinsworth of the Environmental Protection Agency (EPA) wrote about various lists and the toxicological concerns (Chapter 20). A survey of NACA members was done several years ago. In order to assess the level of use of the inerts of toxicological concern at that time, we focused on 54 inert ingredients classified by the EPA as being of toxicological concern. These ended up on the list, with modification, mentioned by Tinsworth. Of the 90 companies we surveyed, 67 responded. We asked five questions: (1) Are inert ingredients being used? (2) Can they be replaced? (3) Will they be replaced in 3 years? (4) Do they serve any purpose? (5) To what extent are they being used? The key results are that six of the 54 inert ingredients were used by six or more firms; 31 were not being used at all; and 17 were used by less than six firms. These results led us to focus attention on the actual extent of use of these "terribly toxic" inert ingredients that we hear so much about. What were the six? Zylene was used by 33 of the respondents, rhodamine B by 16, formaldehyde by 15, methylene chloride by 15, isophorene by 8, and methyl chloroform by 6. Some of these, e.g., methyl chloroform and zylene, have since been moved from the list of highest toxicological concern into List 2. That development began to give focus to the action of solvents, i.e., the main ones on that list that are now used. We asked about the replacement question. Here is the answer to that. Basically, the industry at the time said that there was a substantial number of responses from pharmaceutical companies. The most concern was expressed over zylene, which was

moved over to the other list, indicating that zylene appeared on that list not because of a new health concern, but because of toxicity to aquatic organisms. NACA supports the general thrust of the 1987 EPA inerts policy. It looks really good now in light of some of the legislative initiatives that can be seen on Capitol Hill, being rather embraced more with open arms than in 1967. It is amazing how attitudes change when things get tougher; nevertheless, from the start we did support the 1987 EPA inerts policy, i.e., the minimal testing across the board for inert ingredients, the setting of priorities of how to deal with the overall situation, and how to deal with new ones. We did have some problems with that policy, and they fell into the category of hazard identification, risk assessment, and labeling. The labeling requirement for List 1, i.e., that "this product contains a toxic inert ingredient (blank)", we feel is just too general. It should be more specific and identify the toxicological properties. Everything is toxic, depending on amount. That statement on anything seems like a minor point, but really is an important one. We should keep our language precise. The hazard identification process should be thorough, rigorous, and open to inspection. We had some issues that were difficult, i.e., relative to the thoroughness, rigor, and ability to extract information that was used to place substances on the first list. Our role in NACA is to make sure that a scientifically sound and open process is practiced, and that individual companies need to deal with the specifics of their adjuvant or inert ingredient — that List 1 inerts, or any list really, with regard to expressing some level of concern should be based on risk assessment, not just hazard identification, which is nothing more than a cause of something at some level. It seems that in the 1987 EPA policy, risk assessment is ignored somewhat. A negligible risk situation should be allowed. This brings us to the last topic, and that is the concept of "threshold of regulation" (T/R) practiced by the Food and Drug Administration for migration of chemicals to food from contact with packaging. T/R policy defines some level of migration of the chemical to food for which no special testing would be required. *Use of these substances below these levels will be exempt from food regulations.* We feel that the T/R policy is applicable to and should be used for adjuvants/inerts used in pesticide products. The EPA's policy acknowledges this where it states that under certain circumstances the EPA may waive some or all of these data requirements. For example, if the applicant can show that the proposed new use pattern of the inert ingredient will result in little or virtually no exposure, then it would be exempt from any of the testing regulatory requirements. However, the level should not be so low that nothing could qualify for exemption, and hopefully the current legislative scene will allow us to proceed along these lines. What does this all really mean? Some existing adjuvants are going to be lost by the number of regulatory processes that have been discussed. People are simply not going to conduct all tests required to bring these products up to everyone's satisfaction, and we are going to hear more as they are tested. Some adjuvants are going to pose some unacceptable risks that are going to cause their removal from the market, and it is going to be more difficult to secure approval for new ones. That is clear from what has happened already; therefore, new adjuvants are going to have to demonstrate clear-cut benefits which present significant new market opportunities. Truly, they are going to have to bring out the best, for the days of "snake oil" are over.

## THE IMPORTANCE OF ADJUVANTS TO THE AGRICULTURAL CHEMICAL INDUSTRY

Warren E. Stickle

### ABSTRACT

Adjuvants are not pesticides. Combined with pesticide mixtures, however, they actually enhance pesticide performance. The use of adjuvant materials, whether they are surfactants, stickers, or extenders, has increased over the last few years. Used as effective management tools, adjuvants improve performance, effectiveness, and consistency and enhance and maximize the desired effect of keeping the pesticide where it is placed. Adjuvants' effects on herbicides include the minimization of chemical losses and the maximization of effects of the chemicals once in contact with the target. Adjuvants can improve fungicide performance as well. Adjuvants are important to the production, application, and marketing of pesticide products.

### IMPORTANCE OF ADJUVANTS

The Chemical Producers and Distributors Association is a voluntary, nonprofit membership association consisting of nearly 70 companies engaged in the manufacture, formulation, distribution, and sale of products used on food, feed, fiber crops, and for lawn, garden, and turf care. This industry provides a vast quantity of adjuvants, including surfactants, stickers, and extenders. These materials added to pesticide mixtures actually enhance the consistency of pesticide performance and improve mixing in the spray tank. Adjuvants are used to customize formulations to meet specific needs and can be tailored for varying environmental conditions. Adjuvant use has been increasing over the years and adjuvants are used in a variety of ways. There are now over 200 Environmental Protection Agency (EPA)-registered pesticides that have specific recommendations for the use of adjuvants. More than 300 companies market adjuvants in the U.S. The companies offer a list of more than 4000 materials. They improve performance, effectiveness, and consistency, and enhance and maximize the desired effect of keeping the pesticide where it is placed.

Some researchers claim that up to 70% of the effectiveness of a pesticide can be dependent on spray application. Yet spray application is perhaps the weakest link in the pesticide chain of events. Pesticide application is, however, the final controllable event in most pest control programs. The efficiency and effectiveness of the application often depend on adjuvants. Studies in Louisiana and Arkansas noted that a good adjuvant could put twice as much insecticide in twice the amount of area.

Spray application is affected by many variables, including pesticide stability, solubility, incompatibility, volatilization, foaming, droplet size, drift, suspension, surface tension, coverage, adherence, penetration, and others. If we can control these variables or optimize them, we will get better results. Adjuvants play the key role in controlling these variables.

The work of adjuvants, like antimicrobial products, is impossible to see. Although one cannot see adjuvants at work, there is every indication that the proper use of adjuvants can substantially increase the activity of spray programs.

Adjuvants perform a lot of different, but important jobs, including wetting, sticking, spreading, foaming, reducing foam, dispersing, reducing spray drift, and enhancing bio-

logical activity. No one product will perform all these adjuvant functions, but different compatible adjuvants can be combined to simultaneously perform multiple functions.

Let us take a moment to look at four of these benefits: (1) increasing uptake of the active constituent, (2) improving retention on the target, (3) increasing persistence, and (4) reducing drift.

Adding a surfactant or small quantities of nonphytotoxic spraying oils has improved uptake. Oil keeps leaf surfaces moist longer, thus allowing more time for the herbicide to penetrate. Oils added to some insecticides have improved the level of control of scale insects on citrus and other crops. Also, better control of the horned citrus bug is achieved by adding oil to diazinon.

Adhering or sticking agents can improve the persistence of a formulation. The sticking quality of certain surfactants has been demonstrated with fungicides in oil application for the control of foliage in bananas. Resistance to rain washing has been improved by formulating wettable powders with amine stearates. Persistence can also be increased by using these same compounds for increasing rain fastness.

Although drifting cannot be eliminated, it can be reduced by adding thickening agents to spray mixtures. Adjuvants of this type include a polysaccharide gum with thixotropic properties and alginate derivatives.

Adjuvants can improve fungicide performance by allowing the fungicide application to spread and increase coverage on plants with waxy leaves. They also protect small droplets and help prevent evaporation. Moreover, adjuvants also appear to aid in penetration of the leaf surface. Research indicates that diseases can be controlled by better coverage. Research on Benlate® and Penetrator 3® over a 4-year period found an increase in soybean yields by an average of 134 to 269 kg ha<sup>-1</sup> by adding 237 ml of Penetrator 3 to the regulator recommendation of 0.56 kg ha<sup>-1</sup> of Benlate.

The same can be said for herbicide applications where adjuvants perform several functions. Adjuvant effects on herbicides generally include minimization of chemical losses and maximization of the effect of the chemical once in contact with the target.

There also appears to be as many herbicide additives on the market as there are herbicides. The most common additives are nonionic surfactants. Surfactants are chemicals that modify the surface tension of spray solutions. They can be used when applying certain herbicides to green foliage. Nonionic surfactants are utilized to influence the wetting and spreading ability of liquids, as well as the mixability of substances. These surfactants are compatible with most pesticides and do not carry an electrical charge that may "short-circuit" the pesticide's activity.

Some formulations will create foam or a frothy head in some spray tanks. Foam suppressors may be used effectively with herbicides, particularly to add to the solution before foam becomes a problem. They also work for trapped air and allow for quicker refilling of spray tanks. Foam suppressors reduce the risk of exposure to toxic pesticides in foam.

Adjuvants are used in pure herbicides to make sure that each drop of water contains nearly identical quantities of the particular herbicide since many pure herbicides are not soluble in water. Those adjuvants used for this purpose include emulsifiers, dispersants, stabilizing agents, and buffering agents.

Adjuvants, however, are not without controversy. There is still much confusion surrounding their use, including vague claims and lax reporting requirements. Although there are thousands of registered pesticide products at the EPA, only about 200 registered pesticides have very specific recommendations on their labels for the use of one or more types of adjuvants. The day may come, and perhaps not far away, when more adjuvants will need to be registered and even more thoroughly tested for efficacy.



Some of the confusion concerning adjuvants comes from the lack of understanding of adjuvant terminology. Some people use the terms "adjuvants" and "surfactants" interchangeably. Although they can refer to the same product, all surfactants are adjuvants, but not all adjuvants are surfactants.

Carefully reading the label can be important. If the label requires you to use a crop oil concentrate, but you use a crop oil, you will not get the expected results. For example, a crop oil concentrate is a petroleum- or vegetable-based product generally containing 15 to 20% surfactant/emulsifier and 80 to 85% oil. It is generally used at 1.8 to 2.3 l ha<sup>-1</sup>. Conversely, crop oil contains 2% emulsifier and 98% oil and is generally applied at a rate of 9.4 l ha<sup>-1</sup>.

Careful selection of the proper adjuvant begins with choosing an adjuvant that was manufactured and marketed for agricultural use. Do not use household detergents with agricultural pesticides because they may interfere with pesticide performance. Make sure that the adjuvant has demonstrated efficacy. One type of adjuvant might be required for a particular use of a pesticide, but another adjuvant may be required for a different use. A particular pesticide may require one or more adjuvants for certain uses, yet many specifically prohibit the use of an adjuvant for other uses.

What works one year may not work the following year due to changes in pesticide formulations, newly labeled tank mixes, or changes in application procedure.

Be careful in reading label claims. There are no "miracle" cures. Bogus claims might include statements such as "keeps spray equipment clean", "causes better root penetration", and "results in more nutrient uptake". It is just as important to know when to use an adjuvant as it is to know when not to use one.

The success of adjuvants is due in large measure to the level of understanding of the applicator in several areas. In order to be effective, it is necessary to take a common sense approach to adjuvants to ensure maximum levels of performance.

It is important to know the life processes of the weed, insect, or disease organism. The applicator must know their reproductive and feeding habits as well as their self-protection mechanisms if any adjuvant is to be truly effective.

Several areas need to be considered when choosing a pesticide. Applicators need to consider the availability of formulations, the economics involved with a particular pesticide, and any peculiarities of a formulation, as well as any limitations, future uses, and cautions in the handling, storage, and disposal of a particular pesticide.

Variable factors exist that can lessen the overall performance of a chemical. Mechanical, physiological, and environmental considerations are interrelated and can affect performance.

All of the above-mentioned characteristics affect adjuvants. While they are indispensable in modern agricultural spraying, applicators must be knowledgeable and careful in their use. All pesticide labels should be consulted before any adjuvant use is determined. Label information generally falls into six categories: (1) labels that require adjuvant use, (2) labels that suggest adjuvant use, (3) labels that prohibit adjuvant use, (4) labels that neither require nor prohibit use, (5) labels that contain a combination of recommendations, and (6) labels that contain specific instructions for tank-mixed products.

In conclusion, the adjuvant-enhanced performance of many agricultural pesticides is well documented. If used as a management tool, knowledgeably and properly, they can improve chemical performance and give better weed kill. They are vitally important to the production, application, and marketing of pesticide products, and will probably remain so for a long time to come.



## ADJUVANTS: KEY ASPECTS OF NEW TECHNOLOGY DEVELOPMENT FOR CROP PROTECTION PRODUCTS

J. F. Stewart

The Crop Protection Institute of Canada (CPIC) is made up of 38 member companies and eight associate companies that represent manufacturers, users, and formulators — the people in the agrichemical industry in Canada. The national head office is in Toronto with an executive staff, and dues (a percentage of sales) are paid to support the full-time staff in Toronto. CPIC really is run by national committees, national standing committees, and chairmen in the various provinces of the various chapters of CPIC throughout the country. I am currently privileged to chair the technical committee of CPIC. Public relations work is done in another committee. A special committee on regulatory review now exists because recently the Minister of Agriculture announced a full registration review process for Canada. CPIC has two members who sit on this committee, along with various other interest groups, considering recommendations to make to the Minister of Agriculture.

Concerning future trends in the country in crop protection, we are all faced with changes in the agricultural, forestry, and industrial sections which are going to present major challenges in the future. John McCarthy of the National Agrichemical Chemicals Association alluded to that earlier (Chapter 21). We are definitely at a crossroads at this time, and it is going to be extremely important in the future, particularly for our relationship to the public in how we sell and use agrichemicals. What are the changes that are taking place, at least in our country? We hear terms such as "sustainable agriculture", "organic farming", and "food safety". Food safety with the public is becoming an increasingly important issue. People want to ensure that their food supply is safe, cheap, and of high quality. CPIC is headed in that direction, i.e., advising provincial people, federal people, and government agencies on food safety. Soil conservation is a big thing in our country. We are losing a tremendous amount of our soil in the western prairies, and something has to be done about it. Water contamination is an issue with us, and we are on the forefront of that issue as well. In order to minimize the environmental load, the province of Ontario has a 2002 program (which is not unlike the program that Denmark has announced) to reduce the total amount of pesticide load used in that province by the year 2002 by 50%, and to minimize user-health risks. In the future, there is going to be an increasing diversity and complexity of the industry that will require cooperation between research and development activities in the federal government, provinces, universities, and industry. This is taking place in Canada at a remarkable speed. Market opportunities in our business in the future are going to center around health and safety as well as resource and environmental considerations. If we are not part of these, we will lose market opportunities. These considerations will be the principal criteria in determining the priorities for our work over the next 5 to 7 years, and it is believed that adjuvants have an important role to play in meeting those needs. We are all quite aware of many examples of what adjuvants can do in our industry. We are particularly interested in things such as reducing the amount of agrichemicals applied. Ontario's program 2002, is the first, hopefully, of other programs that will follow in all the other provinces. Adjuvants to enhance the effect of agrichemicals will gain in favor and expand in use.

Millions of pesticide containers are now being stored at municipal collection sites in the western provinces. This has been done for 4 years, and these containers must be disposed of in an environmentally safe way. In November 1988, our association announced a program

by which our industry is collecting one dollar per container, and this is based on the number of containers sold. Money collected throughout the manufacturing industry is distributed equally among the three prairie provinces — Alberta, Saskatchewan, and Manitoba — for the purpose of container disposal. We are not fully there yet in terms of how we intend to recycle these containers, but at least we have set up a mechanism by which we monitor and coordinate the collection of the containers and show responsible care. A product called Merge®\* has been introduced which will reduce the number of containers used in the western provinces in its markets by some 78%. Hopefully, this is the kind of thing that is going to happen more and more in the future.

The idea of adding two or more active ingredients in lower amounts through the use of adjuvants to do the same job as one larger amount of active ingredient obviously has an impact on lessening the environmental load. Many companies do this already, and there will be more and more of this in the future. Our association represents 38 member companies and 8 associates, and they are totally committed to responsible care of their products. CPIC is a communicator or is in the information business and translates concerns. We hear from the public and users, federal agencies, and provincial agencies, and we try to respond very quickly. More needs to be done in this direction, particularly with the idea of bringing technology to the user quickly and safely. This is not always easy to do in the kind of regulatory climate that is in Canada. This criticism is directed toward the regulators, not to the law. There is legislation in Canada that is a bit unlike legislation in the U.S. under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). The U.S. has really reasonable risk and risk/benefit in their legislation; Canada does not. We have merit safety in value and we regulate our pest control program (PCP) act under five different agencies. The main agency responsible for this is Agriculture Canada and the government's and the regulators' hands are really tied primarily by the act. The act states that you have to have a product of merit that is useful in the country; i.e., it has to have value. We are required to submit an efficacy package with all our products in Canada. We are required to register all our adjuvants, including surfactants, and this can become a very burdensome and awkward process. The pesticides directorate in Agriculture Canada in Ottawa has some 60 staff members, compared to 600 in the U.S. Environmental Protection Agency (EPA). They have 6000 products involving 442 active ingredients. A lot of the active ingredients in Canada are the same as in the United States. Agriculture Canada does not have the resources to handle a speedy, safe, effective turnover for the registration of products. It is a challenge to our association to make sure we have the use of adjuvants and technology that are turned over to the user safely and effectively in a very fast and expedient way. The turn-around time in Ottawa to register a product for an active ingredient, on average, is 3 to 4 years. A routine label change takes 14 to 15 months, and a solvent or specification change takes something on the order of 6 to 8 months, merely for the paperwork involved, because the bureaucracy is simply overwhelmed and overburdened. In fact, among those 6000 products, it is stated that they currently have a backlog of 3000 products in Agriculture Canada in one form or another. Whether it deals with label change or specification change, this has become very, very costly. Having the best technology available to compete with not only in your province and country, but also the world, is essential for farmers, and farming is becoming very, very costly in Canada. Ideally, Canada and the U.S. will be able to harmonize their regulatory requirements. A harmonization committee for free trade under Article 708 is meeting with U.S. and Canadian authorities to harmonize registration requirements between the two countries. Part of that harmonization is the fact that we must have some chemistry and residue harmonization between Canada and the U.S. We import, export, and exchange a

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lot of crops together, and your growth is ours. Our association supports research and development efforts and information exchange in the area of adjuvant research. We talked at the First International Symposium on Adjuvants for Agrichemicals, and that was a big step in this direction. It brought people together from all kinds of disciplines and the trend is truly encouraging. It is a compliment to the organizing committee of this second symposium on the number of people in attendance and the representation from around the world. Drs. Grant and Chow have also called for the establishment of an international science journal to publish research on adjuvants, and that is heartily endorsed. Some things such as simple user-brochures that can very easily be put together for use by farmers, foresters, and horticultural people would also be extremely beneficial. CPIC is available for assistance in these matters any time in the future.

## Chapter 24

**INFLUENCE OF TEMPERATURE AND RELATIVE HUMIDITY  
ON THE PERFORMANCE OF THIFENSULFURON WITH  
VARIOUS SURFACTANTS**

J. P. Reed, F. R. Hall, and S. K. Rick

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## I. INTRODUCTION

Changes in environment can influence the phytotoxicity of both soil and foliarly applied herbicides. Relative humidity and temperature are two parameters that affect the phytotoxicity of a herbicide.<sup>2</sup>

Both the microclimate and morphology of the leaf surface influence the persistence and absorption of the herbicide. In general, humidity accelerates the absorption of a herbicide by preventing the desiccation of droplets and simultaneously maintains cuticular permeability. High humidity (90%) is responsible for increased absorption of glyphosate [*N*-(phosphonomethyl) glycine], resulting in greater bermudagrass [*Cynodon dactylon* (L.) Pers.] mortality.<sup>4</sup>

High temperatures before and after spraying increase herbicide penetration through the plant cuticle. However, high temperatures may enhance the desiccation of spray droplets to a point where herbicide penetration ceases. Barban (4-chloro-2-butenyl-3-chlorophenylcarbamate) was more phytotoxic to wild oats (*Avena fatua* L.) at low than at high temperatures.<sup>4</sup>

The addition of surfactant may enhance the uptake and subsequent phytotoxicity of a herbicide. Addition of crop oil concentrate to bentazon {3-(1-methylethyl)-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide} improved weed control under low-humidity conditions.<sup>8</sup> Ritter and Coble<sup>9</sup> observed that the addition of a nonionic surfactant increased the phytotoxicity of acifluorfen {5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid} to common cocklebur (*Xanthium strumarium* L.). Thifensulfuron {3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid} is a sulfonylurea herbicide used for broadleaf weed control in soybean [*Glycine max* (L.) Merr.]. Translocation studies have indicated that sulfonylurea herbicides are ambimobile.<sup>1</sup> Hence, cuticular penetration of these herbicides is an important factor in their efficacy. Nalaweja and Woznica<sup>7</sup> reported that high humidity contributed to greater control of kochia (*Kochia scoparia* Schrod.) by another sulfonylurea herbicide, chlorsulfuron {2-chloro-*N*-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide}. Further, the addition of a nonionic surfactant increased the phytotoxicity of chlorsulfuron applications made in low-humidity conditions.

The objectives of this research were to examine the influence of relative humidity and temperature on the phytotoxicity of thifensulfuron and surfactant applications on two soybean cultivars and three weed species.

## II. MATERIALS AND METHODS

Two soybean cultivars, Asgrow 1937 and Williams 82, were planted 2.0 cm deep, while velvetleaf (*Abutilon theophrasti* Medik.), ivyleaf morningglory [*Ipomea hederacea* (L.) Jacq.], and common lambsquarters (*Chenopodium album* L.) were planted 1.0, 2.0, and 0.5 cm deep, respectively, in a potting soil mixture of Hoyetville sandy clay loam, sand, and peat compost (1:1:1, v/v/v) contained in 1-l plastic pots. Plant densities were established by thinning both soybean cultivars to two plants per pot, six velvetleaf per pot, nine ivyleaf morningglory per pot, and nine common lambsquarters per pot. Water and full-strength nutrient solution were applied to the soil surface on a daily basis. The growth stages when soybean cultivars and weed species were placed in growth chambers were: soybean, 1-2 trifoliolate; velvetleaf, four-leaf stage; ivyleaf morningglory, one- to two-leaf stage; and common lambsquarters, two- to four-leaf stage.

All flats containing three pots of each species were held for 24 h under the following conditions before and after treatment: 30°C at 80% relative humidity (RH), 30°C at 35% RH, 15°C at 80% RH, and 15°C at 35% RH. Treatments consisted of thifensulfuron alone



TABLE I  
Fresh Weights of Soybeans and Broadleaf Weeds under Temperature and Relative Humidity Holding Conditions: Overall Thifensulfuron Treatments

Holding condition*	Fresh weight (g)				
	Asgrow 1937	Williams 82	Velvetleaf	Ivyleaf morningglory	Common lambsquarters
30°C 80% RH	1.23	1.65	0.15	0.87	0.14
30°C 35% RH	2.32	2.49	0.23	0.66	0.12
15°C 80% RH	0.92	1.52	0.09	0.71	0.10
15°C 35% RH	0.75	1.49	0.12	0.79	0.13
LSD (0.05)	0.08	0.08	0.04	0.07	0.04

\* RH, relative humidity.

or combined with 0.25% X-77, 0.125% X-77, 28% N, 0.25% X-77 plus 28% N, or 0.125% X-77 plus 28% N. Approximately 0.07 g of 75% DF formulation of thifensulfuron was diluted with 1 l of water to make treatment solutions that were equivalent to the field application rate of 4 g of active ingredient (a.i.) per hectare based upon 76-cm row spacings. Surfactant mixes consisted of 2.50 ml/l of X-77 for 0.25% X-77, 1.25 ml/l of X-77 for 0.125% X-77, and 40 ml/l 28% N for fertilizer treatments. A spray chamber was used to apply the treatments to flats containing the soybean cultivars and weed species. An 8002 flat-fan nozzle traveled at 3.2 km/h operating at 345 kPa.

Flats held under the various conditions for 24 h were moved to the greenhouse, where sunlight was supplemented with metal halide lights for a 16-h day length. Harvest of plants for fresh weights was initiated 14 d after treatment. Data were analyzed based upon fresh weights as a split-split plot design. Main plots were the holding conditions, subplots were thifensulfuron treatments, and the herbicide by holding condition was the sub-subplot. There were six replicates of each treatment for each soybean cultivar and weed species in the study. Mean separation was performed by the least significant difference method at the  $p = 0.05$  level.

### III. RESULTS AND DISCUSSION

Fresh weight-combined over all thifensulfuron treatments are presented in Table 1. Fresh weights of both soybean varieties were reduced under lower application temperature, and low humidity conditions favored control of ivyleaf morningglory, while velvetleaf was largely unaffected. Application conditions did not appear to affect control of common lambsquarters.

Fresh weights of soybeans and weeds treated with thifensulfuron and adjuvant combinations under all application temperature and RH conditions are presented in Table 2. Asgrow 1937 treated by thifensulfuron + 0.125% X-77 did not vary significantly from untreated checks. However, all thifensulfuron treatments decreased the fresh weight of Williams 82. Velvetleaf growth was significantly reduced by all thifensulfuron treatments, with 0.25% X-77 treatments the most effective. Ivyleaf morningglory treated with thifensulfuron alone had greater fresh weights than treatments with additives, but was not significantly different from thifensulfuron + 0.25% X-77. Both 28% N and surfactant combinations demonstrated the greatest reduction in common lambsquarters growth. The addition of 28% N to thifensulfuron + 0.125% X-77 reduced the fresh weights of common lambsquarters significantly. Although not significant, a similar trend was observed when 28% N was added to thifen-

TABLE 2  
Fresh Weights of Soybeans and Broadleaf Weeds Treated with Thifensulfuron or  
Thifensulfuron-Adjuvant Combinations: Overall Temperature and Relative  
Humidity Holding Conditions

Treatment	Fresh weight (g)				
	Asgrow 1937	Williams 82	Velvetleaf	Ivyleaf morningglory	Common lambsquarters
Thifensulfuron alone	1.29	1.61	0.17	0.84	0.14
Thifensulfuron + 28% N	1.33	1.62	0.13	0.70	0.16
Thifensulfuron + 0.25% X-77	1.23	1.51	0.07	0.76	0.08
Thifensulfuron + 0.125% X-77	1.43	1.80	0.16	0.64	0.16
Thifensulfuron + 0.25% X-77 + 28% N	1.21	1.76	0.09	0.66	0.01
Thifensulfuron + 0.125% X-77 + 28% N	1.11	1.63	0.12	0.66	0.05
Water	1.54	2.18	0.26	1.05	0.25
LSD (0.05)	0.12	0.13	0.05	0.08	0.07

sulfuron + 0.25% X-77. Fresh weights of ivyleaf morningglory were higher with thifensulfuron alone than with other treatments, but were not significantly higher than with thifensulfuron + 0.25% X-77.

In Table 3, thifensulfuron treatment by environmental holding conditions are presented as the percent of control fresh weights. Irrespective of thifensulfuron treatments, Asgrow 1937 growth was affected more than Williams 82 by lower temperatures. Velvetleaf control was significantly greater with thifensulfuron + additives than alone. Better control was achieved when thifensulfuron was applied with 0.125% or 0.25% X-77 surfactant. Neither the addition of 28% N nor manipulation of temperature decreased velvetleaf control. Mersie and Foy<sup>5</sup> observed that more <sup>14</sup>C-chlorsulfuron was absorbed by intact velvetleaf leaves at lower pH levels of 2.4 and 3.4 than at 5.6. Perhaps the higher temperatures coupled with the herbicide-surfactant treatments on the velvetleaf leaf surface initiated some subtle decrease in pH. Since thifensulfuron is amphoteric by nature, a lowering of pH from 6 to 5 would correspondingly decrease H<sub>2</sub>O solubility from 2400 to 24 ppm, which could markedly increase the penetration of thifensulfuron into velvetleaf and subsequently increase phytotoxicity. Ivyleaf morningglory control was greatest at 30°C and 80% RH. However, these environmental conditions are ideal for the growth of ivyleaf morningglory. No significant differences were observed between the 0.125% and 0.25% X-77 surfactant treatments. The addition of 28% N did not increase ivyleaf morningglory control. Although fresh weight reductions were observed for ivyleaf morningglory, no mortality was observed, but stunting was prevalent. Higgins et al.<sup>3</sup> observed the same stunting response in pitted morningglory (*I. lacunosa* L.) and ivyleaf morningglory to acifluorfen, fomesafen {5-[2-chloro-4-(trifluoromethyl)phenoxy]-*N*-(methylsulfonyl)-2-nitrobenzamide}, and lactofen {(+)-2-ethoxy-1-methyl-2-oxoethyl-5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-dinitrobenzoate} that was observed with thifensulfuron and various surfactants in our study.

Common lambsquarters fresh weight was reduced by all treatments and holding conditions except thifensulfuron alone at 30°C, thifensulfuron + 0.25% X-77 at 30°C and 35%

TABLE 3  
Summary of Plant Fresh Weights for Thifensulfuron (with and without Adjuvants)  
and Holding Condition Interactions

Herbicide treatment	Holding condition*	Fresh weight (g)				
		Asgrow 1937	Williams	Velvetleaf (% of control)	Ivyleaf morningglory	Common lambsquarters
Trifensulfuron	30°C 80% RH	64	88	66	65	47
	35% RH	114	72	73	104	83
	15°C 80% RH	78	75	60	71	57
	35% RH	68	64	56	88	68
Thifensulfuron + 0.25% X-77	30°C 80% RH	65	69	41	80	21
	35% RH	122	107	17	58	51
	15°C 80% RH	68	45	28	77	63
	35% RH	41	53	26	68	10
Thifensulfuron + 0.125% X-77	30°C 80% RH	64	90	11	38	6
	35% RH	140	107	190	86	10
	15°C 80% RH	89	67	40	77	115
	35% RH	60	65	39	61	160
Thifensulfuron + 0.25% X-77 + 28% N	30°C 80% RH	66	85	60	43	3
	35% RH	94	100	20	49	3
	15°C 80% RH	87	71	8	93	0
	35% RH	62	66	52	77	0
Thifensulfuron + 0.125% X-77 + 28% N	30°C 80% RH	54	73	70	35	3
	35% RH	94	104	60	42	3
	15°C 80% RH	82	73	0	88	0
	35% RH	54	49	48	96	105
Trifensulfuron + 28% N	30°C 80% RH	66	60	44	30	108
	35% RH	122	111	67	105	45
	15°C 80% RH	89	43	40	68	37
	35% RH	58	30	39	88	37
LSD (0.05)		24	26	11	11	15

\* RH, relative humidity.

RH, thifensulfuron + 0.125% X-77 at 15°C treatments, thifensulfuron + 0.125% X-77 + 28% N at 30°C and 35% RH, and thifensulfuron + 28% N at 30°C and 80% RH, which were not significantly different from the untreated check. Although better common lambsquarters growth was observed with high temperatures, a rate response of X-77 was observed under these conditions which led to the best control of any treatment. The addition of 0.25% X-77 to thifensulfuron resulted in significantly better control at lower temperatures. The use of 28% N and X-77 in combination with thifensulfuron significantly reduced common lambsquarters fresh weights.

#### IV. CONCLUSIONS

In general, the addition of either X-77 or 28% N to thifensulfuron resulted in better weed control. Ideal soybean growth conditions, 80°C and 35% RH prior to the application of thifensulfuron adjuvant combinations, resulted in superior weed control. Recovery by the susceptible cultivar, Asgrow 1937, was greater when growing conditions were ideal.

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## Chapter 25

EFFECT OF HUMECTANTS ON PESTICIDE UPTAKE THROUGH  
PLANT LEAF SURFACES

S. Matsumoto, S. Suzuki, H. Tomita, and T. Shigematsu

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## ABSTRACT

The biological activity of herbicides (2,4-D and urea-type experimental herbicide) and fungicides (phthalide and amide-type experimental fungicide, etc.) was examined in the presence or absence of humectant (glycerine or sodium lactate). Depending on the concentration or the type of humectant incorporated, the pesticides showed different activities. The effect of humectants on pesticide uptake through plant leaf surfaces is discussed in relation to the moisture enhancement and water solubility changes of pesticides by incorporating the humectants.

## I. INTRODUCTION

Pesticide uptake through plant leaf surfaces has been a great concern for formulation scientists.<sup>8</sup> Studies on the mechanism of pesticide penetration through plant cuticle have been reviewed in the literature.<sup>2,3,6</sup> In those studies, Fick's first law is commonly used for analysis of the mechanism. According to Fick's first law, the concentration of a solute in water outside the cuticular membrane is the driving force for the transcuticular movement.

Figure 1 shows the schematic procedure of pesticide uptake through plant leaf surfaces. Pesticides repeat drying and wetting effect on the leaf surface after being sprayed. Then, precipitation and dissolution of the pesticide in the retained water takes place. The dissolved part of the pesticide must be used for the successive penetration pathway. Therefore, the function of water retained on the leaf surface is thought to be very important for pesticide uptake.

There have been many reports on pesticide uptake in relation to relative humidity using labeled compounds.<sup>4,5</sup> Humectants have also been examined for uptake studies of pesticides<sup>1,9</sup> or fertilizers.<sup>7,10</sup> However, actual moisture retained in the formulated pesticide has not been precisely examined yet, and the incorporation of humectants sometimes had negative effects on the uptake.

In this chapter, we will discuss (1) the extent to which pesticide activity depends on the retained water (equilibrium moisture), (2) the extent to which humectants enhance the retention of moisture in the pesticides dried after spraying, (3) how actual pesticidal activity may be affected by the incorporation of humectants, and (4) what other side effects will appear by the incorporation of humectants.

## II. MATERIALS AND METHODS

### A. PESTICIDES

For herbicidal activity tests, 2,4-D [(2,4-dichlorophenoxy)acetic acid] and urea-type experimental herbicide (urea herbicide) were used. The 2,4-D formulation was a 90% soluble powder (SP) which is commercially available (Nissan Chemical Ind., Ltd.). The urea herbicide was formulated in our laboratory into 50% wettable powder (WP), 25% suspension concentrate (SC) and 4% dust (D). The particle size of the active ingredient in WP, SC, and D was 2.7, 3.1, and 2.8  $\mu\text{m}$ , respectively.

For the fungicidal activity test, the following commercial fungicides and amide-type experimental fungicide (amide fungicide) effective against rice sheath blight were used: pen-cycuron 25% WP (Kumiai Chemical Ind. Co., Ltd.): rice sheath blight; flutolanil 25% WP (Nissan Chemical Ind., Ltd.): rice sheath blight; and phthalide 20% WP (formulated in our laboratory): rice blast.

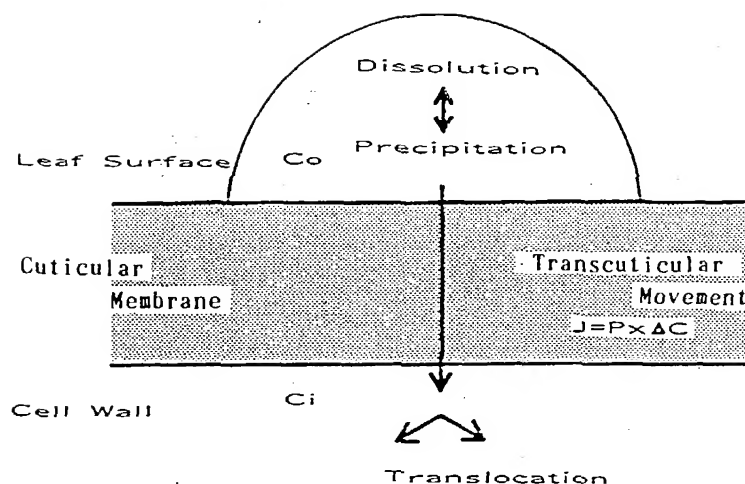


FIGURE 1. Schematic representation of pesticide uptake through plant leaf surfaces.

## B. HUMECTANTS

Humectants used for the experiments were glycerine, ethylene glycol, propylene glycol, sodium lactate, polyethylene glycol (mw 400, Toho Chemical Ind. Co., Ltd.), polyvinyl alcohol (GOHSENOL NL-05, Nippon Gohsei Chemical Ind., Ltd.), and sodium polyacrylate (AQUAKEEP 10SH, Seitetsu Chemical Ind., Ltd.).

## C. HERBICIDAL ACTIVITY TESTS

### 1. Effect of Humidity

Three urea herbicide formulations (WP, SC, and D) were used for the herbicidal activity test. Each test solution was sprayed on the leaf surface of common cocklebur (*Xanthium strumarium* L.) (2-leaf stage) and velvetleaf (*Abutilon theophrasti*, Medicus) (3-leaf stage) at doses from 0.19 to 4.0 kg a.i./ha. Treated plants were separately kept for 3 h in the different growth chambers where the humidity was controlled at 20 and 90% RH, respectively. Leaves of the plants were then washed with sufficient water to remove the remaining herbicide on the leaf surface. The test plants were finally moved to the greenhouse and the herbicidal activity was measured 3 weeks after treatment.

### 2. Effect of Humectants

The urea herbicides WP and 2,4-D were used for this experiment. Each herbicide spray solution was applied on the leaf surface of *X. strumarium* (three-leaf stage) at dosages of 0.125 to 2.0 kg of active ingredient (a.i.) per hectare, with or without humectant (glycerine or sodium lactate) in the spray solution. The amount of humectant added to the spray solution was 0.5 or five times that of each herbicide formulation. The sprayed plants were air dried and then kept in a growth chamber at 70% RH. Herbicidal activity was measured 3 weeks after treatment.

## D. FUNGICIDAL ACTIVITY TESTS

### 1. Effect of Humidity

The amide fungicides penicuron and flutolanil were used for this experiment. Each test solution was sprayed on rice (*Oriza sativa* L.) plant leaves at doses of 20, 40, and 80 g a.i./10A (area unit of a standard Japanese paddy field). The rice plants were separately kept

for 18 h in different growth chambers at 50 and >90% RH, respectively. After washing the leaf surface with sufficient water, the inoculation was carried out by spraying the mycelial suspension of *Rhizoctonia solani*. Fungicidal activity was measured 7 d after inoculation.

## 2. Effect of Humectants

Spray solutions of phthalide (10, 50, and 100 ppm) were applied on the leaf surface of rice plants (four-leaf stage), with or without humectant (glycerine or sodium lactate) in the solution. After drying by air stream for 1 h, rice plants were kept for 17 h in the growth chamber at >90% RH. The surfaces of the rice leaves were then wiped with acetone-soaked cotton to remove the remaining fungicide on the leaves. Inoculation was carried out by spraying the spore suspension of *Pyricularia oryzae*. Fungicidal activity was measured 5 d after inoculation.

## E. MOISTURE ANALYSIS

### 1. Equilibrium Moisture in the Pesticide Dried after Spraying

Three formulations of urea herbicide (WP, SC, and D) were used for this experiment. Each spray solution was dried in an open petri dish for 6 h at 60% RH and 20°C. The moisture content of the residual solid was measured with a Karl Fisher moisturemeter.

### 2. Effect of Humectants on the Equilibrium Moisture

The WP formulation of the urea herbicide was used for the experiments. The spray solution of the WP containing humectant was air dried for 3 h in an open petri dish. The dish was kept at 20°C in a chamber where humidity was controlled. After 48 h, equilibrium moisture was analyzed with a Karl Fisher moisturemeter. The kind and amount of humectant as well as the humidity of the chamber were changed throughout the series of experiments.

## F. WATER SOLUBILITY ANALYSIS

Technical urea herbicide and 2,4-D were used for this experiment. In a 30-ml glass sample tube, 100 mg of technical herbicide and a water solution of humectant were mixed. The sample tube was shaken by a mechanical shaker for 48 h at 25°C. The suspension mixture was then filtered with 0.45- $\mu$ m plastic paper filter. The concentration of the technical herbicide in the filtrate was analyzed by HPLC. The concentrations of the humectants, glycerine and sodium lactate, in water were changed from 0 to 50%.

## III. RESULTS AND DISCUSSION

### A. EFFECT OF MOISTURE ON THE BIOLOGICAL ACTIVITY OF PESTICIDES

Moisture effect was examined for fungicides and a herbicide by changing the RH under which sprayed plants were kept for the time necessary for the uptake of pesticides.

Figure 2 shows the effect of moisture on the fungicidal activity of amide fungicide, penicuron, and flutolanil against rice sheath blight. All three fungicides showed higher activity at higher humidity conditions at any fungicide dosage. The difference in activity between humid conditions and dry conditions was large, especially at lower dosages.

Similar results were observed in herbicidal activity tests of the three formulations (D, WP, and SC) of the urea herbicide, as shown in Figure 3: for all three formulations, higher herbicidal activity was observed at higher humidity conditions. In this figure, herbicidal activity is indicated by the mean 90% control dosage ( $I_{90}$ ) of the herbicide against two weed species (*X. strumarium* and *A. theophrasti*). Therefore, the lower value corresponds to the higher activity.

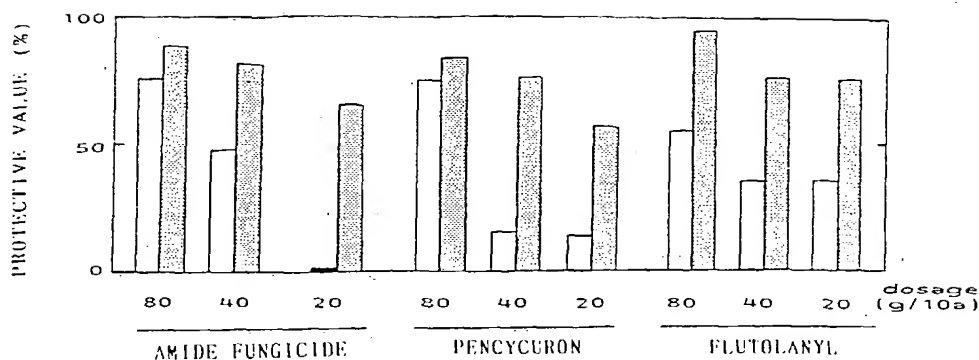


FIGURE 2. Moisture effect on the fungicidal activity of three fungicides (amide fungicide, pencycuron, and flutolanil) against rice sheath blight. White bar, dry condition (RH 50%); shadow bar, humid condition (RH >90%).

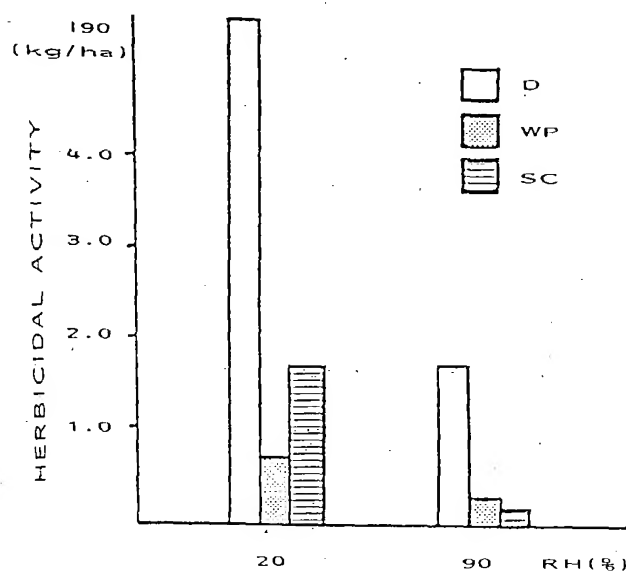


FIGURE 3. Moisture effect on the herbicidal activity of the urea herbicide against two weed species: *Xanthium strumarium* L. and *Abutilon theophrasti* Medicus; formulation types: dust (D), wettable powder (WP), and suspension concentrate (SC); herbicidal activity: mean value of  $I_{50}$  against two weeds.

The results of the above two experiments clearly suggest that the moisture level on the leaf surface is very important for pesticide uptake by the plant.

#### B. EQUILIBRIUM MOISTURE OF SPRAYED PESTICIDES

Figure 3 also indicates the differences in activity among the three formulations at both humidity conditions. The dust formulation showed especially low activity. The particle size of the a.i. in each formulation is almost the same (2.7 to 3.1  $\mu\text{m}$ ). Therefore, the difference in activity must be due to other reasons.

The equilibrium moisture of these formulations was measured when the spray solutions were dried at 60% RH and 20°C. The result is shown in Figure 4, in which the dust formulation (D) revealed the lowest amount of equilibrated moisture. This fact could explain the relatively low activity of the dust among the three formulations.

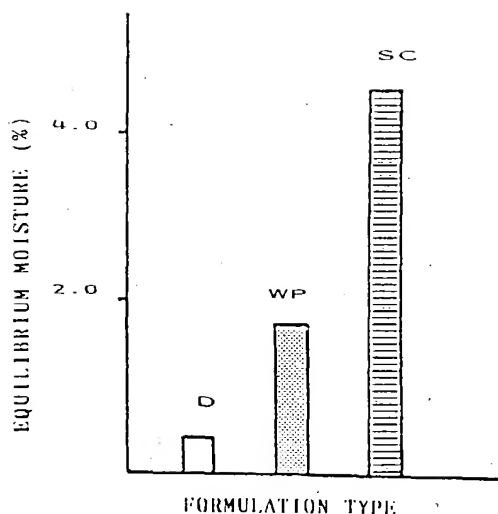


FIGURE 4. Equilibrium moisture content of the three formulations of the urea herbicide when the spray mixture was dried at 60% RH and 20°C. Moisture content measurement: Karl Fisher moisturemeter; formulation types: dust (D), wettable powder (WP), and suspension concentrate (SC).

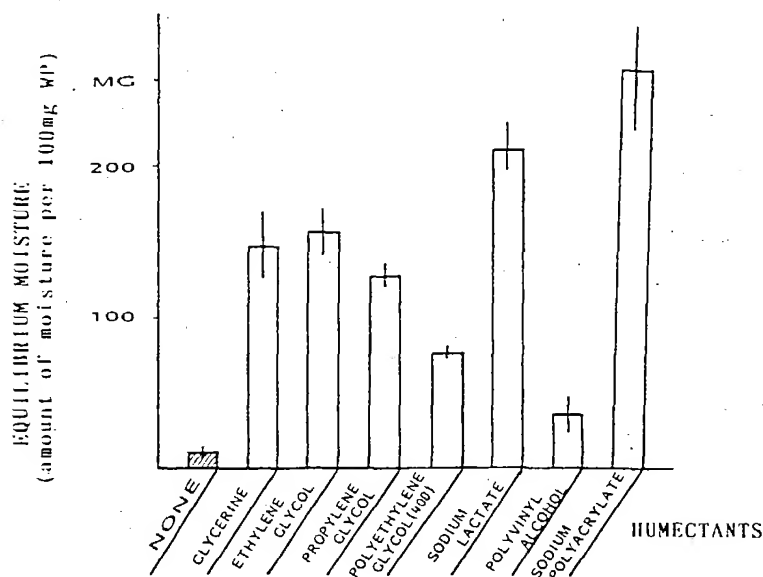


FIGURE 5. Effect of humectants on the equilibrium moisture of the urea herbicide WP formulation when the spray mixture was dried at 90% RH and 20°C.

### C. EFFECT OF HUMECTANTS ON THE EQUILIBRIUM MOISTURE

It was suggested in the previous examples that moisture is very important for pesticide uptake (activity). Therefore, adjuvants which may enhance the equilibrium moisture content of pesticides (humectants) were screened.

Figure 5 shows the effect of various humectants on the equilibrium moisture of the urea herbicide (WP formulation) dried under 90% RH when the amount of each humectant added



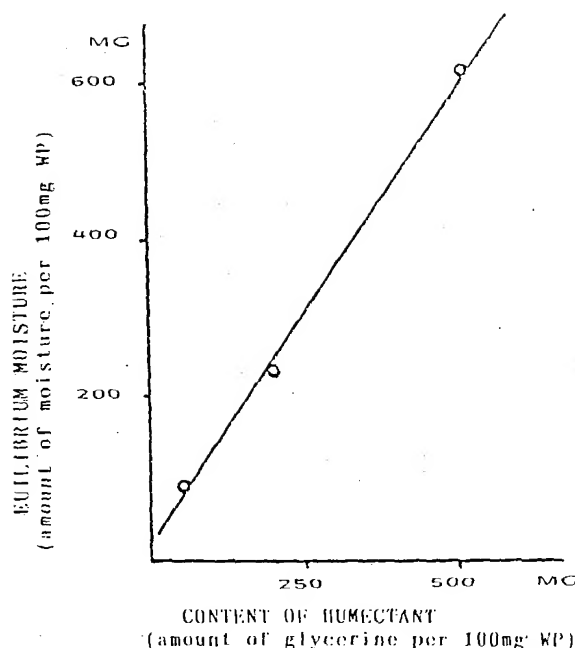


FIGURE 6. Relationship between the amount of humectant added to the spray mixture and the equilibrium moisture of the urea herbicide WP formulation after drying at 90% RH and 20°C.

was half the weight of the WP in the spray solution. Most humectants showed a remarkable enhancement of the equilibrium moisture of the WP. Among these humectants, polyols such as glycerine or ethylene glycol, sodium lactate, and polyacrylate were found to have high moisture-enhancing potency.

Next, the relationship between the amount of humectant added in the spray solution and the equilibrium moisture content in the pesticide was examined using glycerine as a humectant. The result is shown in Figure 6, where we note that the equilibrium moisture increases linearly in proportion to the amount of glycerine.

The equilibrium moisture content of the pesticide was further examined by changing the humidity in the presence or absence of humectants in the spray solution. As shown in Figure 7, incorporation of glycerine into the solution greatly enhances the equilibrium moisture, especially at high humidity conditions.

#### D. EFFECT OF HUMECTANTS ON THE BIOLOGICAL ACTIVITY OF PESTICIDES

In the previous examples, it was found that humectants have remarkable moisture-enhancing potency. Therefore, their effect on actual biological activity was examined.

Figure 8 shows the fungicidal activity of phthalide against rice blast in the presence or absence of humectants in the spray solution. It was found that both glycerine and sodium lactate increase the activity of phthalide, particularly at lower dosages of the fungicide.

The effect of humectants on herbicidal activity was examined for the urea herbicide and 2,4-D using glycerine and sodium lactate as humectants (Figure 9). In the case of glycerine, both herbicides showed higher activity compared with the case of no humectant. On the other hand, sodium lactate showed almost the same, or rather low, activity compared with the no-humectant case.

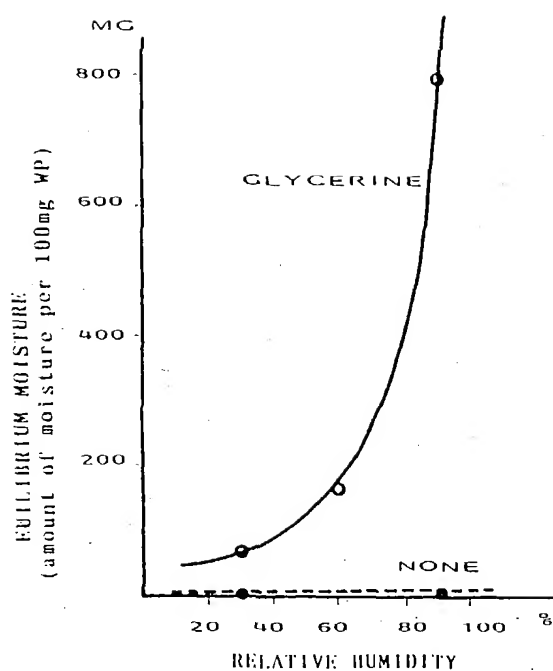


FIGURE 7. Relationship between the humidity and the equilibrium moisture of the urea herbicide WP formulation in the presence or absence of glycerine. Amount of glycerine added to the spray mixture was half the weight of the WP.

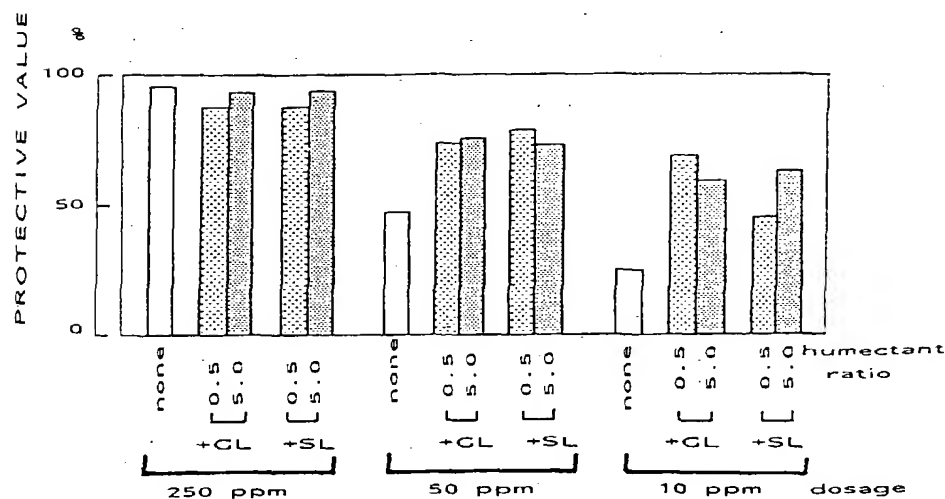


FIGURE 8. Effect of humectants on the fungicidal activity of phthalide against rice blast. +GL, glycerine; +SL, sodium lactate.

The above results with sodium lactate in the herbicidal activity test is inconsistent with the moisture-enhancing potency of this humectant (Figure 5). Therefore, the incorporation of this humectant must result in some factor against activity.

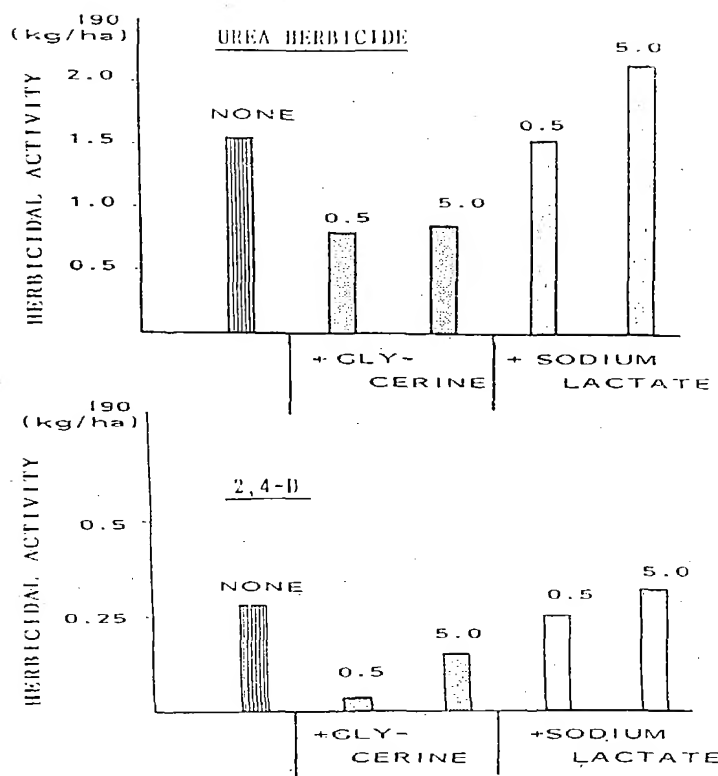


FIGURE 9. Effect of humectants on the herbicidal activity of the urea herbicide and 2,4-D against *Xanthium strumarium* L.

#### E. OTHER EFFECTS OF HUMECTANTS

To investigate the cause of the above inconsistency, the solubility change of the previous herbicides in the humectant-water solution was measured by changing the concentration of humectant in the solution.

In the case of glycerine, the solubility of each herbicide keeps almost the same value as the basic water solubility while the humectant concentration increases, although the urea herbicide gradually increases its solubility at high humectant concentrations (Figure 10).

On the other hand, sodium lactate greatly lowers the solubility of both herbicides, particularly at high humectant concentrations. The sprayed pesticide solution will gradually lose water on the leaf surface after spraying. When a humectant is contained in the solution, its concentration will increase in proportion to the water loss of the sprayed solution.

From these considerations, it is thought that one of the reasons for low herbicidal activity in the case of sodium lactate incorporation must be its negative side effect on the solubility of pesticides in the sprayed solution.

There could be some other unknown factors caused by the incorporation of humectants, since all the biological responses which have been shown so far cannot be explained only by the equilibrium moisture or the pesticide solubility change. For example, the relationship between biological activity and the amount of humectant is still unclear. Therefore, further investigation of pesticide uptake in the presence of humectants is necessary.

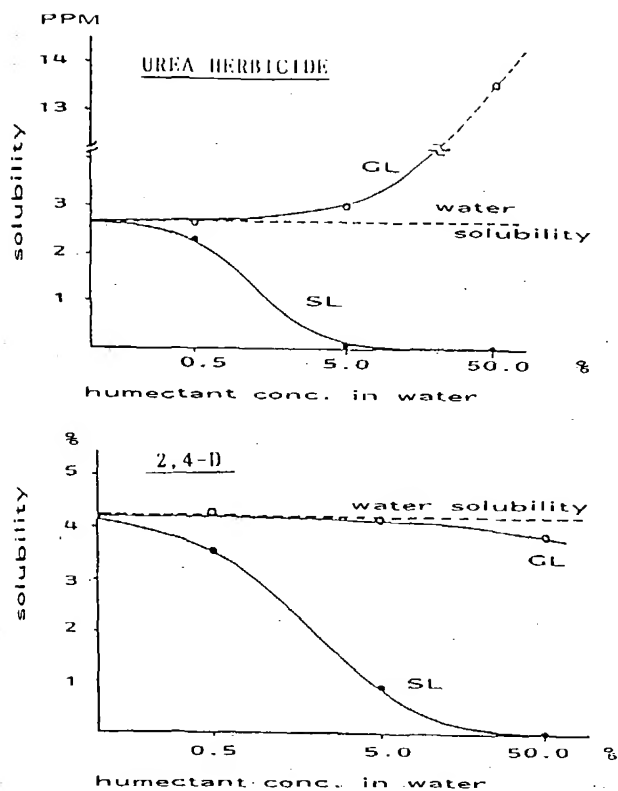


FIGURE 10. Solubility change of the urea herbicide and 2,4-D in the humectant-water solution. GL, glycerine; SL, sodium lactate.

#### IV. CONCLUSIONS

1. The biological activity of pesticides depends on moisture.
2. Equilibrium moisture retained in the pesticides dried after spraying is affected by the type of formulation.
3. Humectants enhance the retained moisture in pesticides.
4. The solubility of pesticides in the sprayed solution is sometimes affected by the incorporation of humectants.

Moisture enhancement and solubility change by humectants are both important factors for the biological activity (uptake) of pesticides in using humectants as spray adjuvants.

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## Chapter 26

**THE INFLUENCE OF ADJUVANTS AND ENVIRONMENT ON  
ABSORPTION AND TRANSLOCATION OF IMAZAQUIN IN  
PITTED MORNINGGLORY [*IPOMOEA LACUNOSA* (L.)]**

G. D. Wills and C. G. McWhorter

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## ABSTRACT

A nonionic surfactant, a petroleum oil-based adjuvant, and a soybean [*Glycine max* (L.) Merr.] oil-based adjuvant were foliarly applied separately with  $^{14}\text{C}$ -radiolabeled ammonium salt of imazaquin {2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl]-3-quinolinecarboxylic acid} herbicide to pitted morningglory (*Ipomoea lacunosa* L.). Treated plants were grown in environmentally controlled growth chambers at several combinations of air temperature and relative humidity (RH). After 48 h, absorption and translocation of the  $^{14}\text{C}$ -herbicide were greater at 95 than at 40% RH and at 35 than at 27 or 18°C. Translocation of the  $^{14}\text{C}$ -radiolabel was often increased by the addition of the nonionic surfactant or the petroleum oil-based adjuvant over that with soybean oil-based adjuvant or with no adjuvant added to the herbicide solutions.

## I. INTRODUCTION

Activator adjuvants are almost always added to foliar-applied herbicides to enhance the level of weed control.<sup>6</sup> The use of surfactant adjuvants to enhance pesticide activity dates back to the late 1800s when an arsenical insecticide was caused to injure plants after soap was added to the spray solution.<sup>3</sup> The use of a surfactant to enhance the herbicidal activity of foliar-applied 2,4-D [(2,4-dichlorophenoxy) acetic acid] was reported in 1942.<sup>15</sup> In 1963, diuron [*N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea] was changed from being only a soil-applied herbicide to a soil- and foliar-applied herbicide by the addition of a surfactant to the spray solution.<sup>4</sup>

Nonionic surfactants are the most widely used adjuvants for foliarly applied treatments where water is used as the carrier for herbicide spray solutions.<sup>5</sup> Other frequently used adjuvants are petroleum oil-based products containing 80 to 83% phyto-bland-oil and 17 to 20% surfactant,<sup>6</sup> and vegetable oil-based products containing 85 to 93% vegetable oil and 7 to 15% surfactant/emulsifier.<sup>2</sup>

Environmental conditions at the time of treatment have a significant effect on herbicidal activity. Absorption and translocation of foliar-applied herbicides were greater at 27 to 35°C than at 18 to 22°C.<sup>7-13</sup> Herbicide movement was also greater at 95 to 100% than at 35 to 45% RH.<sup>9-13</sup>

Pitted morningglory is among the most troublesome weeds in the southeastern U.S.<sup>1</sup> Imazaquin selectively controls pitted morningglory when applied postemergence in soybeans,<sup>14</sup> but control is often erratic. Experiments reported here investigate the herbicidal activity of imazaquin on pitted morningglory as affected by adjuvants and environmental conditions at the time of treatment.

## II. MATERIALS AND METHODS

### A. GREENHOUSE PROCEDURES

Pitted morningglory was grown in the greenhouse in 10-cm diameter plastic pots containing a 1:1 mixture of Bosket sandy loam (Molic hapludalf) and sand. Pots were watered two or three times daily. At the time of treatment, plants were approximately 3 weeks old with four to five true leaves. The greenhouse was maintained at 30 to 40°C day and 23 to 30°C night temperatures, 40 to 75% RH, and 13 to 14 h of sunlight per day.

### B. $^{14}\text{C}$ -IMAZAQUIN PREPARATIONS

Radiolabeled  $^{14}\text{C}$ -imazaquin was labeled in the carboxyl position and had a specific activity of 20  $\mu\text{Ci/mg}$ .  $^{14}\text{C}$ -imazaquin was converted to the water-soluble ammonium salt

with equimolar ammonium hydroxide. The imazaquin acid was added to a solution containing approximately two thirds the equimolar amount of ammonium hydroxide. The solution was further titrated to pH 9 with ammonium hydroxide to ensure solubilization. The solution was titrated back to pH 7.5 with glacial acetic acid to ensure stabilization of the herbicide.

#### C. $^{14}\text{C}$ -TREATMENT SOLUTIONS

The stock solution of  $^{14}\text{C}$ -imazaquin was diluted to the radioactivity of 0.1  $\mu\text{Ci}$  in 10  $\mu\text{l}$  in four different adjuvant combinations, including 0.25% Tween 20 (polyoxyethylene 20 sorbitan monolaurate), 1.25% petroleum oil adjuvant, Atplus 411F [polyoxyethylene sorbitan fatty acid ester:mineral oil (17:83, w/w)], 1.25% soybean oil adjuvant [emulsifier:soybean oil fully refined (15:85, w/w)], and water alone (no adjuvant).

#### D. $^{14}\text{C}$ -IMAZAQUIN TREATMENTS

$^{14}\text{C}$ -Imazaquin was applied in the amount of 0.1  $\mu\text{Ci}$  in 10  $\mu\text{l}$  to a 2-cm<sup>2</sup> area on the upper surface at the apex of the third true leaf from the bottom of four- to five-leaf pitted morningglory plants. During treatment, the ambient temperature of the laboratory was maintained at the same level as the growth chambers for that experiment. Immediately upon drying of the herbicide solution on the surface of the treated leaf, plants were placed into growth chambers at 18, 27, or 35°C, each at 40 or 95% RH. Plants were maintained under a 14-h light period for 48 h. Growth chambers contained both incandescent and fluorescent lights with a photosynthetic photon flux density of 550  $\text{E m}^{-2} \text{s}^{-1}$ .

#### E. $^{14}\text{C}$ -ANALYSIS

The  $^{14}\text{C}$  remaining on the leaf surface was determined by excising the treated section, placing it into a 20-ml vial containing a 4 ml solution of methanol:water (1:1) and swirling for 5 s on a test tube stirrer. The treated section was then lifted above the solution using tweezers and rinsed with three 2-ml volumes of solution which was added to the original wash solution to provide a total of 10 ml. A 100- $\mu\text{l}$  aliquot was combusted in a biological material oxidizer and analyzed in a liquid scintillation spectrometer. This procedure was conducted twice for each treated leaf section. The data were summed for the two washes.

Absorption into the treated leaf was calculated as that amount of the applied  $^{14}\text{C}$  not recovered in the washes. After the unabsorbed and/or adsorbed  $^{14}\text{C}$  was washed from the surface, the radioactivity remaining within the treated section was determined by similarly combusting the treated section. The data were corrected for background and dilution factors and expressed as percent counts per minute of a standard of the same quantity of radioactivity as was applied for each herbicide-adjuvant combination. Distribution of  $^{14}\text{C}$  was determined by autoradiographic techniques where 0 was equal to no color and 100% was equal to complete coverage of the plant portion.

The experiment was arranged as a randomized complete block in a split plot design, with combinations of temperature and humidity being the whole plot factors and herbicide mixtures being the subplot factors. Each herbicide subplot was replicated five times and the experiment was repeated over time.

### III. RESULTS AND DISCUSSION

Absorption was consistently greater at 35°C than at lower temperatures and better at 95 than at 40% RH (Table 1). Each adjuvant was effective in increasing absorption over that with no surfactant. Tween 20 resulted in significantly higher absorption at 95% RH (50 to 95%) than at the 40% level (15 to 24%). The petroleum oil-based adjuvant increased absorption under both high and low RH at 27 and 35°C, but only under high humidity at

TABLE 1  
Absorption and Translocation of  $^{14}\text{C}$ -Imazaquin in  
Pitted Morningglory after 48 Hours

Temp. (°C)	RH (%)	No adjuvant	Tween-20	Petro-oil adjuvant	Soy-oil adjuvant
Absorption (%)					
18	40	9 cd	15 c	17 d	28 b
	95	28 b	50 b	46 c	29 b
27	40	3 d	15 c	58 bc	29 b
	95	20 bc	61 b	69 b	39 b
35	40	3 d	24 c	59 bc	39 b
	95	63 a	91 a	82 a	65 a
Remaining in the Treated Leaf (%)					
18	40	1 b	6 c	7 b	9 b
	95	7 b	25 b	20 ab	11 b
27	40	2 b	9 c	25 a	10 b
	95	9 a	39 a	20 ab	14 b
35	40	2 b	14 bc	30 a	30 a
	95	7 a	25 b	21 ab	36 a
Translocated Out of the Treated Leaf (%)					
18	40	7 c	9 c	10 c	18 a
	95	21 b	26 b	26 bc	18 a
27	40	1 c	6 c	33 b	20 a
	95	11 bc	22 b	49 ab	25 a
35	40	2 c	10 c	29 bc	9 b
	95	56 a	67 a	61 a	29 a

Note: Within columns at each location of  $^{14}\text{C}$ , numbers followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

18°C. Soybean oil-based adjuvant was the least effective, with increased absorption occurring only under low RH.

The trend for the applied  $^{14}\text{C}$  to remain within the treated leaf correlated with the absorption data. There were greater amounts of  $^{14}\text{C}$  remaining in the treated leaf when surfactant was added. The amounts of  $^{14}\text{C}$  in the treated leaf were increased at high humidity with no surfactant and with Tween 20 at 27 and 35°C, but not with the petroleum or soybean oil-based adjuvants.

Translocation of the radioactivity from the treated area was often greater at 95% RH. This was most pronounced at the highest temperature (35°C).

The percent coverage of the radiolabel on autoradiographs is shown in Table 2. Where movement was into the shoot above the treated leaf, Tween 20 resulted in the greatest movement at the higher temperatures and high relative humidity. Movement was also increased with the petroleum oil-based adjuvant at the higher temperatures, but with no significant difference in movement between low and high RH.

This same trend held true for movement into the shoot below the treated area, but with less amounts going into the more mature tissues of the plant. Movement into the roots was greatly increased by high humidity. Both Tween 20 and petroleum oil-based adjuvant increased translocation at 27 and 35°C.

TABLE 2  
Autoradiograph Coverage by  $^{14}\text{C}$ -Imazaquin Applied to  
Pitted Morningglory after 48 Hours

Temp. (°C)	RH (%)	No adjuvant	Tween-20	Petro-oil adjuvant	Soy-oil adjuvant
Shoot Above the Treated Leaf (%)					
18	40	3 b	4 e	4 c	1 d
	95	16 b	19 d	22 c	20 bc
27	40	1 b	14 de	49 b	13 cd
	95	41 a	71 b	64 ab	35 b
35	40	13 b	50 c	66 ab	34 b
	95	53 a	90 a	75 a	63 a
Shoot Below the Treated Leaf (%)					
18	40	1 c	3 c	1 d	1 c
	95	9 c	9 c	12 cd	10 bc
27	40	1 c	6 c	31 bc	6 bc
	95	21 b	43 b	43 ab	16 b
35	40	4 c	36 b	53 a	17 b
	95	32 a	68 a	57 a	46 a
Roots (%)					
18	40	0.4 c	1.4 b	1.0 c	0.3 b
	95	4.0 bc	7.8 b	7.1 bc	5.3 ab
27	40	0.1 c	2.3 b	18.5 ab	5.0 ab
	95	13.9 a	35.0 a	24.4 a	8.5 a
35	40	1.1 c	11.5 b	20.0 a	5.4 ab
	95	8.1 ab	46.3 a	28.8 a	8.8 a

Note: 0, no color; 100%, complete coverage. Within columns at each portion of the plant, numbers followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

### ACKNOWLEDGMENT

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## Chapter 27

DISPOSITION AND DISSIPATION OF DROPLETS APPLIED  
AERIALY USING PENETRATOR®

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\* This paper represents original research and refers to no prior published works. A list of other articles on aerial application is included for those interested in reading about other work accomplished in the field.

## ABSTRACT

Deposition of low-volume sprays into a cotton canopy can be improved by adding Penetrator® (West Helena, AK). A spray volume of 9.34 l/ha with Penetrator at 0.59 l/ha gave an increase of about 64% over water alone. Changing the spray volume to 28.07 l/ha gave the largest increase, and a comparable increase was seen when Penetrator was added at this spray volume. Penetrator rates as low as 0.30 l/ha in a spray volume of 9.34 l/ha increased the area of coverage by approximately 37%. Dissipation of droplets from an altitude of 6.1 m showed a straight-line relationship with water alone. When Penetrator was added at 0.59 l/ha in a spray volume of 18.7 l/ha, the rate of droplet dissipation was less than for water alone. Correlation coefficients of height by droplet density or height by area covered for Penetrator were 0.59 and 0.44, respectively. Compared to water alone at nearly the same conditions, the correlation coefficients were 0.89 and 0.83, respectively. Thus, Penetrator may aid in protecting the droplets from evaporation.

## I. INTRODUCTION

Evaporation, simply defined, means to change a liquid (or solid) into a vapor. From experience, everyone knows that water placed in an open container decreases in volume upon standing. When this occurs, we say that evaporation has taken place and can be explained in terms of the motion of molecules. At any given temperature above absolute zero, the molecules of a liquid move — some slowly, some at intermediate rates, some very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbors and escape, i.e., evaporate, to the space above the liquid. This activity continues until a dynamic equilibrium exists where the vapor and liquid below it are in balance with each other, i.e., evaporation and condensation cease to occur.

Several factors affect evaporation, such as temperature, relative humidity (RH), size of droplet or body, purity of the material, etc. Temperature, as it changes, causes an increase or decrease in molecular activity and thus affects the rate of evaporation. RH, as it decreases or increases, affects evaporation; and mixtures of compounds affect evaporation. The vapor pressure of a solution containing a nonvolatile substance or a substance of low volatility (oils or solids) is lower than that of the pure liquid. This can be reversed by mixing highly volatile materials such as alcohols, esters, etc. with water, which changes the molecular activity (slowing it down when adding an oil or speeding it up when adding an alcohol or other material).

What we are concerned with is a droplet of material (usually water and pesticide) reaching the target to which it is directed. As an aerial applicator travels across a field at a high rate of speed, the material he is spraying (droplets) has numerous forces working on it. Size of the droplet, temperature, RH, and other factors come into play. With this knowledge, some adjuvants can be useful tools in the control of evaporation. The material we have experimented with is Penetrator, an emulsified, highly refined mineral oil with no obvious phytotoxicity.

## II. MATERIALS AND METHODS

### A. 1986 LOW-VOLUME SPRAY STUDY

#### 1. Treatments

- Water check applied, 9.34 l/ha
- Penetrator (6.25%, v/v) applied, 9.34 l/ha

- Water check applied, 28.07 l/ha
- Penetrator (2.10%, v/v) applied, 28.07 l/ha

## 2. Application Method

- Aircraft AGCAT B; swath width, 18.3 m
- Air speed 144 to 152 km/h
- Number of nozzles 26
- Type For 9.34 l/ha, D4-56  
For 28.07 l/ha, D8-56

## 3. Conditions at Application

- Temperature 33.5°C average, 39% RH
- Range 45 to 32%
- Time of applications 1:00 to 5:00 p.m.
- Wind NE at 6.4 km/h, occasional gusts to 16 km/h

## 4. Deposition Data

Water-sensitive paper was placed on metal stakes in a cotton canopy at 30.5, 61, and 91 cm above the soil. Twenty-five stakes were spread over a distance of 183 m at about 5.8 m apart in the drill of a row of cotton. Cotton rows were on 0.965-m centers with a 1.98-m skip between every other row. Twenty-five samples were collected at each level. Droplets per square centimeter and percent area covered were determined using a Compac Image Analyzer System.

## B. 1987 AND 1988 DISSIPATION OF DROPLETS FROM 6.1 METERS

### 1. Treatments 1987

Water check applied, 18.7 l/ha  
Penetrator (3.125%, v/v) applied, 18.7 l/ha

### 2. Conditions at Application

- Water, 18.7 l/ha; temperature, 28.3°C; RH, 90%; time, 9:15 a.m. CDT
- Water, 18.7 l/ha; temperature, 33.3°C; RH, 68%; time, 10:00 a.m. CDT
- Water, 18.7 l/ha; temperature, 34.4°C; RH, 60%; time, 11:30 a.m. CDT
- Penetrator (3.125%, v/v) 18.7 l/ha; temperature 36.7°C; RH, 56%; time, 1:20 p.m. CDT

### 3. Treatments 1988

Water check applied, 18.7 l/ha  
Penetrator (3.125%, v/v) applied, 18.7 l/ha

### 4. Conditions at Application

- Water, 18.7 l/ha; temperature, 26.7°C; RH, 80%; time, 9:00 a.m. CDT
- Water, 18.7 l/ha; temperature, 30.6°C; RH, 72%; time, 10:00 a.m. CDT
- Water, 18.7 l/ha; temperature, 32.8°C; RH, 60%; time, 12:00 P.M. CDT
- Penetrator (3.125%, v/v), 18.7 l/ha; temperature, 32.8°C; RH, 60%; time, 12:15 p.m. CDT

### 5. Application Method

- Aircraft Air Tractor; swath width, 21.4 m
- Air speed 200 to 208 km/hr
- Number of nozzles 53
- Type Whirl jet 8s, alternated with 5s

TABLE 1  
Deposition into a Cotton Canopy by a 9.34 l/ha Spray  
Volume with and without Penetrator<sup>a</sup>

Canopy level	Droplets/cm <sup>2</sup>		% Area covered	
	Penetrator <sup>b</sup>	Water	Penetrator	Water
91 cm	20.6	12.7	1.105	1.011
61 cm	16.7	5.4	0.804	0.349
30.5 cm	7.4	4.8	0.380	0.207

<sup>a</sup> 1986 low-volume spray study.

<sup>b</sup> Penetrator rate: 0.59 l/ha, 6.25% (v/v).

TABLE 2  
Canopy Deposition of 28.07 l/ha Spray Volume with and  
without Penetrator<sup>a</sup>

Canopy level	Droplets/cm <sup>2</sup>		% Area covered	
	Penetrator <sup>b</sup>	Water	Penetrator	Water
91 cm	43.4	33.5	4.681	3.086
61 cm	26.0	14.9	2.411	1.148
30.5 cm	13.9	11.2	1.036	0.527

<sup>a</sup> 1986 low-volume spray study.

<sup>b</sup> Penetrator rate: 0.59 l/ha (8 fl. oz/A), 2.10% (v/v).

## 6. Deposition Data

Droplets per square centimeter and percent area covered were determined using a Compac image analyzer system. The aircraft was flown along each side and above three 6.1-m towers. The towers were approximately 9.1 m apart. Water-sensitive paper was attached every 0.30 m from 0.305 to 3.05 m, and every 0.61 m from 3.66 to 6.1 m.

## III. RESULTS AND DISCUSSION

### A. DEPOSITION OF DROPLETS FROM LOW-VOLUME SPRAYS INTO A COTTON CANOPY

Penetrator increased the canopy deposition of both 9.34 l/ha and 28.07 l/ha spray volumes over water alone, increasing both droplets per square centimeter and percent area covered. At the 61- and 91-cm levels, adding Penetrator to a spray volume of 9.34 l/ha increased droplet density to 20.6 and 16.7 droplets per cm<sup>2</sup>, respectively (Table 1). Water alone had a maximum density of 12.7 droplets per cm<sup>2</sup> at the 91-cm level. The percent area covered by adding Penetrator was nearly twice that for water alone at the 30.5- and 61-cm levels.

When Penetrator was added to a 28.07 l/ha spray volume, droplet density surpassed that of 9.34 l/ha at all levels in the canopy by a minimum of 6.5 droplets per cm<sup>2</sup> (Table 2). As with the 9.34 l/ha spray volume, the area covered at the 30.5- and 61-cm levels when Penetrator was added was approximately twice the area covered by water alone.

Increasing the spray volume from 9.34 to 28.07 l/ha increased droplet density. However, the percent increase was less when Penetrator was added compared to water alone. Increasing the spray volume and adding Penetrator increased droplet density by 210, 160, and 190% at the 30.5-, 61-, and 91-cm levels, respectively (Table 3). Increasing the spray volume



TABLE 3  
Effect of Spray Volume on Droplets/cm<sup>2</sup> at Three Levels  
within a Cotton Canopy<sup>a</sup>

Canopy level	Penetrator <sup>b</sup>			Water		
	9.34 (l/ha)	28.07 (l/ha)	% inc	9.34 (l/ha)	28.07 (l/ha)	% inc
91 cm	20.6	43.4	210	12.7	33.5	260
31 cm	16.7	26.0	160	5.4	14.9	270
30.5 cm	7.4	13.9	190	4.8	11.2	230

<sup>a</sup> 1986 low-volume spray study.

<sup>b</sup> Penetrator rate: 0.59 l/ha at 9.34 l/ha (6.25%, v/v) and 28.07 l/ha (2.10%, v/v).

TABLE 4  
Effect of Spray Volume on Percent Area Covered at  
Three Levels within a Cotton Canopy<sup>a</sup>

Canopy level	Penetrator <sup>b</sup>			Water		
	9.34 (l/ha)	28.07 (l/ha)	% inc	9.34 (l/ha)	28.07 (l/ha)	% inc
91 cm	1.105	4.681	420 <sup>c</sup>	1.011	3.086	310
61 cm	0.804	2.411	300	0.349	1.148	330
30.5 cm	0.380	1.036	270	0.207	0.527	250

<sup>a</sup> 1986 low-volume spray study.

<sup>b</sup> Penetrator rate: 0.59 l/ha at 9.34 l/ha (6.25%, v/v) and 28.07 l/ha (2.10%, v/v).

<sup>c</sup> Significantly greater than water alone.

without adding Penetrator increased droplet density by 260, 270, and 230% at the 30.5-, 61-, and 91-cm levels, respectively.

By increasing the spray volume from 9.34 to 28.07 l/ha and adding Penetrator, the percent area covered increased significantly compared to water alone. However, only at the 91-cm level was the percent increase significantly different from water alone (Table 4).

In 1987, a similar study was conducted using Penetrator at 0.30 l/ha with a spray volume of 9.34 l/ha and at 0.59 l/ha with a spray volume of 18.7 l/ha. The temperature was 35°C, RH averaged 26%, and there were little, if any, wind currents. Under these conditions, Penetrator at 0.59 l/ha and a spray volume of 18.7 l/ha increased deposition by 28, 22, and 55% at the 30.5-, 61-, and 91-cm levels respectively. The most satisfactory performance was at 0.59 l/ha with a spray volume of 28.07 l/ha.

#### B. DISSIPATION OF DROPLETS AT LOW VOLUMES IN 1987 AND 1988

Dissipation of droplets from a spray volume of 18.7 l/ha was analyzed by regression analysis. Droplets sprayed from an altitude of 6.1 m without Penetrator dissipated with height. The rate of dissipation was a function of temperature and RH. The rate (b) of droplet dissipation and the high correlation coefficient (r) between height and droplet density or percent area covered for water alone indicates a near straight-line relationship (Table 5). In 1987, when Penetrator was added, the rate of dissipation was the lowest (Figure 1) and the correlation coefficients were 0.59 and 0.44 for height by droplets per square centimeter and

TABLE 5  
Correlation Coefficients (r) from Regression Analysis of Droplet Deposition  
Applied at 18.7 l/ha from 6.1 m with and without Penetrator (1987 and 1988)

	Conditions at application		Droplet density (cm <sup>2</sup> )			% Area covered		
	Temp (°C)	RH (%)	Rate	r	p > t	Rate	r	p > t
1987 Treatment								
Water	28.3	90	2.03	0.94	0.001	0.19	0.85	0.001
	33.3	68	1.16	0.93	0.001	0.11	0.87	0.001
	34.4 <sup>a</sup>	60	1.03	0.89	0.001	0.09	0.83	0.001
Penetrator <sup>b</sup>	36.7 <sup>a</sup>	56	0.80	0.59	0.020	0.07	0.44	0.100
1988 Treatment								
Water	26.7	80	1.64	0.78	0.001	0.07	0.48	0.070
	30.6	72	3.49	0.813	0.001	0.21	0.74	0.001
	32.8 <sup>c</sup>	60	2.66	0.953	0.001	0.32	0.92	0.001
Penetrator <sup>b</sup>	32.8 <sup>c</sup>	60	1.59	0.833	0.001	0.13	0.41	0.131

<sup>a</sup> Treatments compared in Figure 1.

<sup>b</sup> Penetrator rate: 0.59 l/ha, 3.125% (v/v).

<sup>c</sup> Treatments compared in Figure 2.

height by percent area covered, respectively. In effect, the regression line flattened when Penetrator was added in 1987.

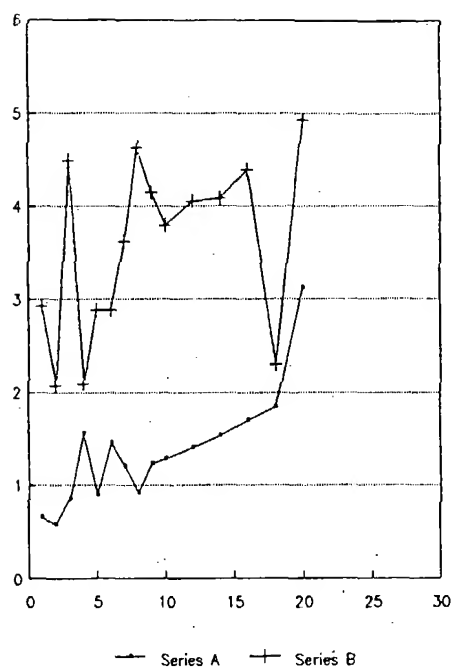
The regression analysis varies somewhat when comparing the 1987 and 1988 data (Table 5). There may have been other climatic variations such as air currents and direction of air movement. For treatment with water alone at 26.7°C (60% RH), the correlation coefficient for percent area covered was 0.48, and 0.41 for Penetrator. The correlation coefficients for the water and Penetrator treatments at 32.8°C, which occurred at 12:00 and 12:15 p.m., respectively, are relatively far apart. The regression line did flatten when Penetrator was added in 1988.

Although a more complete study of temperature and RH is needed to fully understand how Penetrator affects droplet dissipation, the data do suggest that Penetrator protects against droplet dissipation. Figure 2 compares an 18.7 l/ha spray volume of water alone with Penetrator at 0.59 l/ha. The conditions at application were nearly identical. Whether this protection is through reducing evaporation or some other physical property is not known, but it does suggest that height above the canopy during aerial application may be less critical if Penetrator is added to the spray solution. We do not advocate pilots flying at 6.1 m above the canopy.

## ACKNOWLEDGMENTS

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## % AREA COVERED



## DROPLETS/sq. cm.

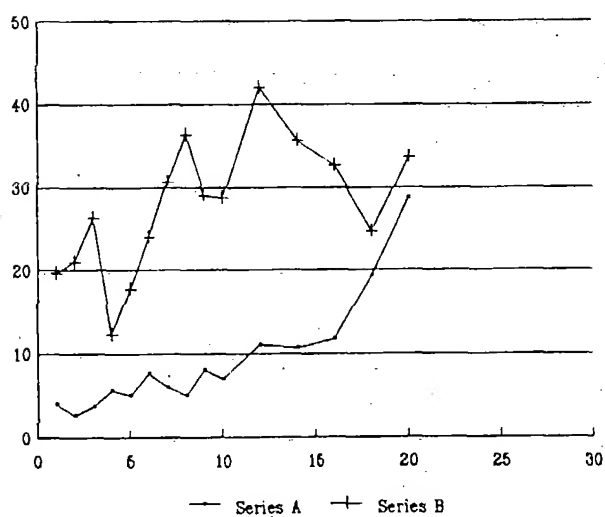


FIGURE 1. Droplet deposition of an 18.7 l/ha spray from 6.1 m without (Series A) and with (Series B) Penetrator. Penetrator application was made at 0.59 l/ha, 36.7°C, and 56% RH. Water (Series A) applied at 34.4°C and 60% RH.

## % AREA COVERED

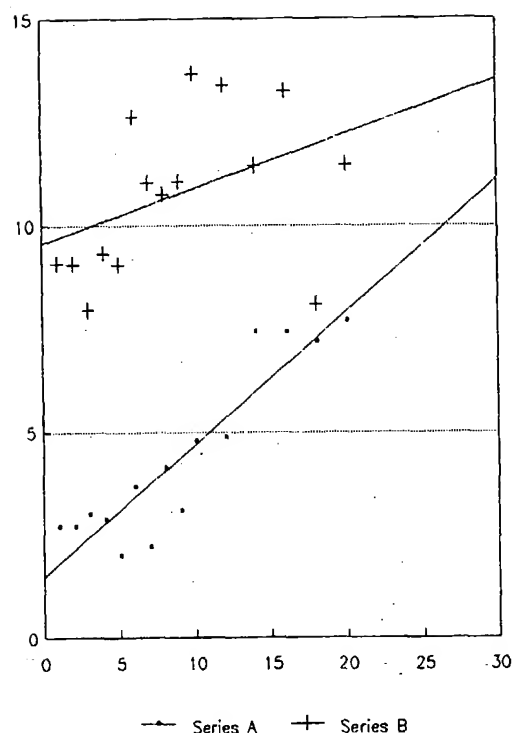


FIGURE 2. Comparison of regression lines of percent of area covered by an 18.7 l/ha spray volume with water alone (Series A) and Penetrator added at 0.50 l/ha (Series B). Conditions at application, 32.8°C and 50% RH; time, 12:00 and 12:15 p.m., CDT, respectively.

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## Chapter 28

SPRAY ATOMIZATION RESPONSES TO AGRICULTURAL  
FORMULATION ADJUVANTS

N. B. Akesson, W. E. Steinke, and D. E. Bayer

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## ABSTRACT

Adjuvants, including surfactants, stickers, and spreaders, are a widely used group of materials commonly a part of every pesticide liquid formulation.<sup>8,11,12</sup> These are also used in many liquid biological formulations such as bacilli and viruses as well.<sup>14</sup> While most of these additives are used to directly affect the pesticidal action of specific active ingredients, a few such as the water-soluble polymers are used for their direct effect on physical properties and, hence, the atomization of the liquid spray.<sup>5</sup> This chapter will examine what effect these additives may have on the physical characteristics of the spray liquid: viscosity, surface tension, density, evaporation rate, and a function of viscoelasticity generally associated with the water-soluble polymer additive. In turn, we will examine how these may be correlated with spray atomization or drop sizes produced by given atomizers.<sup>2</sup>

## I. INTRODUCTION

In Chapter 33<sup>3</sup> of the proceedings of the First International Symposium on Adjuvants for Agrochemicals, physical property data were presented on a variety of formulations of pesticides which had been studied by agricultural engineers and weed control personnel at the University of California, Davis. The objectives of these test procedures were to try and determine how various additives could be used to (1) alter atomization characteristics, (2) provide better adherence of active chemicals to plants, and (3) reduce the hazards of drift loss from treated crops as well as liftoff or airborne transfer following an application, which results in small but finite amounts of pesticide moved by the ambient airflow. This work has been continued with additional correlation of physical formulation characteristics and spray atomization extended to several new formulations, particularly of biopesticides.

## II. MATERIALS AND METHODS

As with our earlier studies, we have attempted to establish in the laboratory the basic physical properties of viscosity, surface tension, density, viscoelasticity, and evaporation rate for all of the material formulations (tank or application mixes) with which we have worked.<sup>10</sup> Additionally, graphic data have been developed to try and rationalize some of these characteristics correlated with the drop sizes and size ranges produced.

Our drop-sizing equipment consisted of two probes and a data analyzer developed and sold by the Particle Measuring Systems Company of Boulder, CO.<sup>15</sup> A model OAP-2D-GA1 imaging probe was used to cover a range of approximately 26- to 2060- $\mu\text{m}$  diameter, while a forward light scatter probe was used to observe and read data in drop sizes from about 0.5 to 100  $\mu\text{m}$ . These probes and allied equipment were used in our wind tunnel (Figure 1).<sup>15</sup>

Shown at the left of Figure 1\* is the air entrance with turbulence control screens (five to eight of these plastic screens of about 18 mesh) and the "bell" reduction section to reduce to the tunnel throat dimensions of 60  $\times$  60 cm. The nozzle under test is shown in the first section, while the 2-D probe is shown in the second section. Air was drawn through the tunnel by an axial flow fan powered by a 200-kW engine. Air velocity can be controlled from about 30 to 210 km/hr. A positioner traverses the atomizer in two dimensions in the throat of the tunnel to obtain a scan of the pattern of released spray.

## III. RESULTS AND DISCUSSION

The basic physical properties of the formulations tested for drop size (including tap water) are shown in Table 1. Here, the viscosity ranges from mPa  $\cdot$  s for water to a maximum

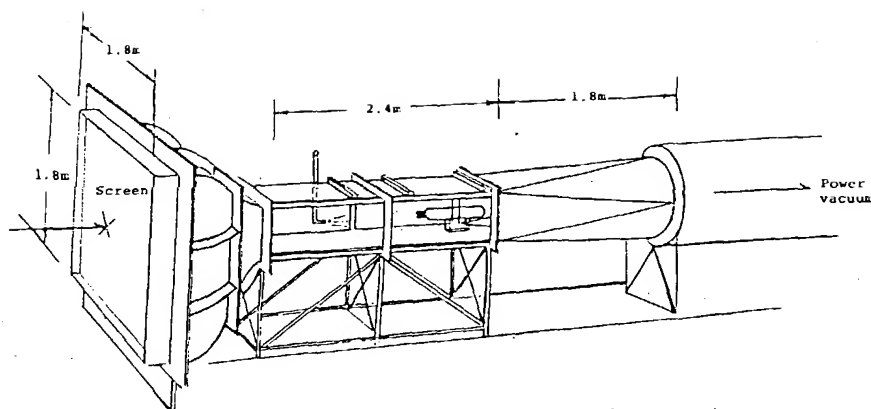


FIGURE 1. Wind tunnel and drop-size probe.

**TABLE I**  
Physical Properties of Formulations Tested for Drop Size

Material (% w/w)	Viscosity (mPa · s)	Surface tension (mN/m)	Density (g/ml)	(T at 20°C)
Water (dist.)	1	72	1	Averaged
CS oil, 85% Pydrin, 15%	19	37.1	0.92	Pyrethroid, fenvalerate
Foray™ 48B	107.4	51.4	1.174	Novo, B.t.
Gypchek™ <sup>a</sup>	2	46.3	1.06	Virus
TMBIO™ <sup>b</sup>	6.5	55.4	1.15	Virus
Molasses (R)	184	42.4	1.32	Refined
Molasses (UR)	1524	56.5	1.39	Unrefined

<sup>a</sup> Gypchek was formulated with 473.8 g of molasses and 227 g of Orzan (lignum sulfate) plus 3078 g of water.

<sup>b</sup> TMBIO had 947.5 g of molasses, 227 g of Orzan, and 2604 g of water.

formulation actually tested of about 107.4 mPa · s at 20°C for a *Bacillus thuringiensis* (Foray 48B™, Novo Labs). The two straight molasses formulations were not tested for drop size. Surface tension varied from a high of 72 mN/m for water to 37 mN/m for a cottonseed oil (85%)-Pydrin (15%) mixture to a low of 35 mN/m for water with 0.25% surfactant (Valent X-100™, FMC Corporation, San José, CA).

Density for the various mixtures did not vary greatly. Straight unrefined molasses was highest at 1.39 g/ml, while the cottonseed oil (CSO)-Pydrin mixture was lowest at 0.92 g/ml.

#### A. DROP SIZES FOR INDIVIDUAL NOZZLES

Typical drop size distribution graphs are shown in Figures 2 through 6 for the specific atomizers and operating conditions stated.<sup>16</sup> Figure 2\* is for tap water from a 24-mm-diameter

\* From Akesson, N. B. and Gibbs, R. E., Pesticide drop size as a function of spray atomizers and liquid formulations, in *Pesticide Formulations and Application Systems*, Vol. 10, Bode, L. E., Hazen, J. L., and Chasin, D. G., Eds., American Society for Testing and Materials, Philadelphia, 1990, 170. With permission.

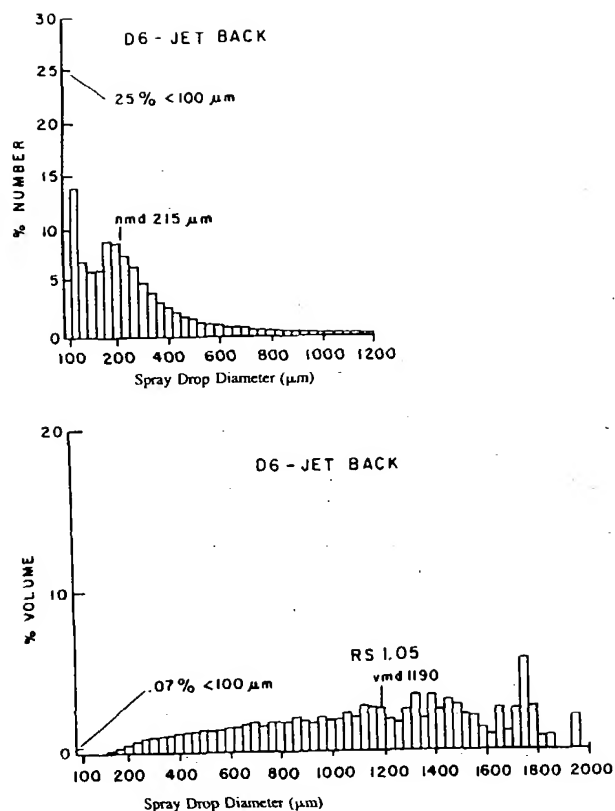


FIGURE 2. Drop-size distribution, 24-mm orifice, 161-km/h airspeed, 276 kPa pressure.\*

straight orifice plate directed at  $0^\circ$  (parallel) or with a 161-km/hr airstream. Liquid pressure was at 276 kPa.<sup>1</sup>

A rather broad distribution of drop sizes can be seen; the volume median diameter (vmd) is 1190  $\mu\text{m}$ , where 50% of the drop mass or volume lies above this size and 50% below. Note also the number graph (top) which shows the distribution by number, with the median at 215  $\mu\text{m}$  or nmd. While only 0.07% (by volume) of the drops were smaller than 100- $\mu\text{m}$  diameter, the number of these small drops is shown to be 25% below the 100- $\mu\text{m}$  diameter.

Figure 3\* shows the effect of turning the orifice or jet nozzle at  $90^\circ$  to the 161-km/hr airstream. The orifice size is somewhat larger at 32-mm diameter, but the effect on drop sizes, both range of sizes and vmd and nmd, is striking. Now the nmd is  $<56 \mu\text{m}$ , while the vmd has dropped to 340  $\mu\text{m}$ .

Figure 4\* shows water spray distribution from a hollow-cone nozzle at  $0^\circ$  to the 161-km/h airstream and operated at 276 kPa water pressure. The #46 core provides the radial velocity to produce the hollow-cone spray pattern. In so doing, the drop size is also significantly reduced; the nmd now is 263  $\mu\text{m}$ , while the vmd is 435  $\mu\text{m}$ .

Figure 5 utilizes a 24-mm orifice and #45 (greater radial force) case to produce still smaller drop sizes of nmd 253  $\mu\text{m}$  and vmd 327  $\mu\text{m}$ . Note how the distribution is narrowed as the drop size produced is smaller. This is primarily a function of the normal or Gaussian distribution. This indicates that as drops become smaller, a greater energy must be available to reduce or break these small drops, while larger drops are still being broken by the available energy.

Nozzle Type..... DE JET  
 Nozzle Angle Rel.  
 to Airstream.....  $90^\circ$   
 Spray Pressure..... 276 kPa  
 Airspeed..... 161 km/h

Distance to Probe... 15 cm  
 Depth of Field..... 1.8 cm  
 Slice Rate..... 3.8 MHz  
 Date..... 04/02/15  
 Time..... 14:58:00  
 File Number..... S.B. 15

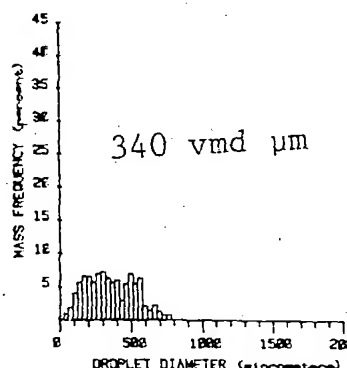
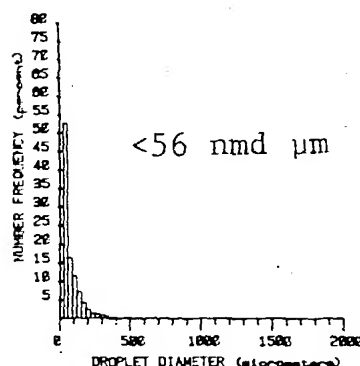
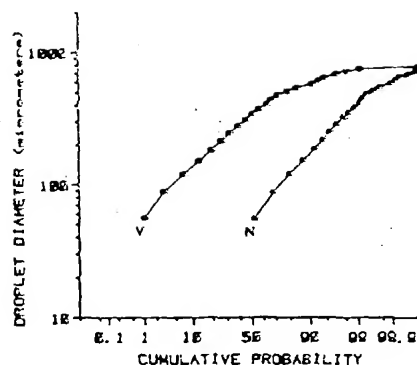


FIGURE 3. Drop-size distribution, 32-mm orifice, 161 km/h airspeed, 276 kPa pressure.\*

Figure 6 shows a rotary screen-type atomizer (Beecomist O™, Telford, PA) operated at 7800 rpm in a 161-km/hr airstream with about 12 l/min liquid (water plus 0.03% Valent X-77). The rotary screen atomizers produce a range of sizes similar to the pressure nozzles of Figures 2 through 5, but the higher energy input plus the added surfactant (note reduction of surface tension, Table 1) reduced drop size significantly to an nmd of  $<56 \mu\text{m}$  and a vmd of  $181 \mu\text{m}$ .<sup>7</sup>

## B. DROP SIZES VS. FLOW RATE

Shown in Figures 7\*, 8\*, and 9\* are data on the effect of the flow rate of water as well as the CSO-solvent mixture on the drop sizes produced.<sup>4</sup>

Figure 7 shows graphs of data on jet or straight orifice nozzles obtained from a series of wind tunnel tests of various flow rates (orifice sizes) at a constant pressure of 276 kPa and 161-km/hr airspeed. The vmd in microns is plotted on the vertical scale, while the flow rate in l/min is on the lower scale. The topmost curve shows water being sprayed at  $0^\circ$  to the airstream. The next lower curve shows the effect of adding a surfactant (Valent X-77 at 0.03%), which reduced the surface tension to 35 mN/m. Viscosity and density are little changed from that of water, but the effect of surface tension reduction is notable. Also shown is the short dashed curve of RD (recirculation)-type nozzles with water at  $0^\circ$  to the air. The lowermost curve shows water spray from the orifice jets at  $90^\circ$  to the airstream.

\* From Akesson, N. B., and Gibbs, R. E., Pesticide drop size as a function of spray atomizers and liquid formulations, in *Pesticide Formulations and Application Systems*, Vol. 10, Bode, L. E., Hazen, J. L., and Chasin, D. G., Eds., American Society for Testing and Materials, Philadelphia, 1990, 170. With permission.



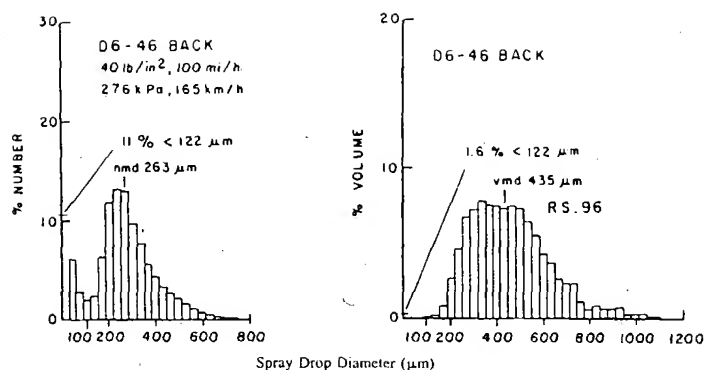


FIGURE 4. Hollow cone, D6, #46 at 0° to 161-km/h airspeed, 276 kPa pressure.\*

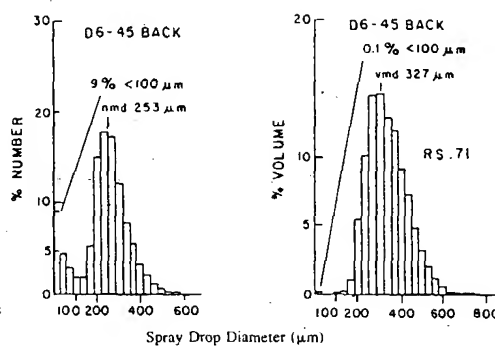


FIGURE 5. Hollow cone, 24-mm orifice, #45 core at 0° to 160-km/h airspeed, 276 kPa pressure.

Figure 8 shows curves of drop size vs. flow rate for hollow-cone nozzles (as do Figures 4 and 5). Here, the topmost curve is for nozzles at 0° to the 161-km/hr airstream, operated at 276 kPa pressure with a CSO (85%) solvent (15%), the latter simulating the Pydrin pyrethroid of Table 1. The next lower curve is for water at 0°, showing the effect of reduced surface tension on the drop size from cone nozzles. Curves below these are for the CSO mix and for water at 90° to the airstream. Here, the greater breakup exposure of the drops produces very nearly the same size distribution from both CSO and water.

Figure 9 shows similar curves developed from multiple tests on fan-type nozzles. Again, water and the CSO mix are compared. The topmost curve is for water at 0° to the 161-km/hr airstream. The curve is for CSO at 45° to the airstream (45° down from 0°). Next is the curve for 90° with water, and then the highly similar curve for 90° with CSO mix. CSO at 0° falls just below these, and the fan nozzles again show the sharp decrease in drop size that results when surface tension is reduced, but only when operated at 0° to the airstream. The lowermost two curves are for fan nozzles operated at 135° (45° forward) to the airstream, which produces the smallest drops due to high-energy air shear.

### C. DROP SIZE VS. VISCOSITY

Figure 10 indicates a typical viscosity response of vegetable oil-based spray to changes in temperature. Viscosity per se does not appear to be a dominant factor in drop-size functions, being more related to flow rate. Thus, it is important when drop-size tests are run to control the flow rate of the system. Figure 11\* shows drop-size data obtained with the wind tunnel

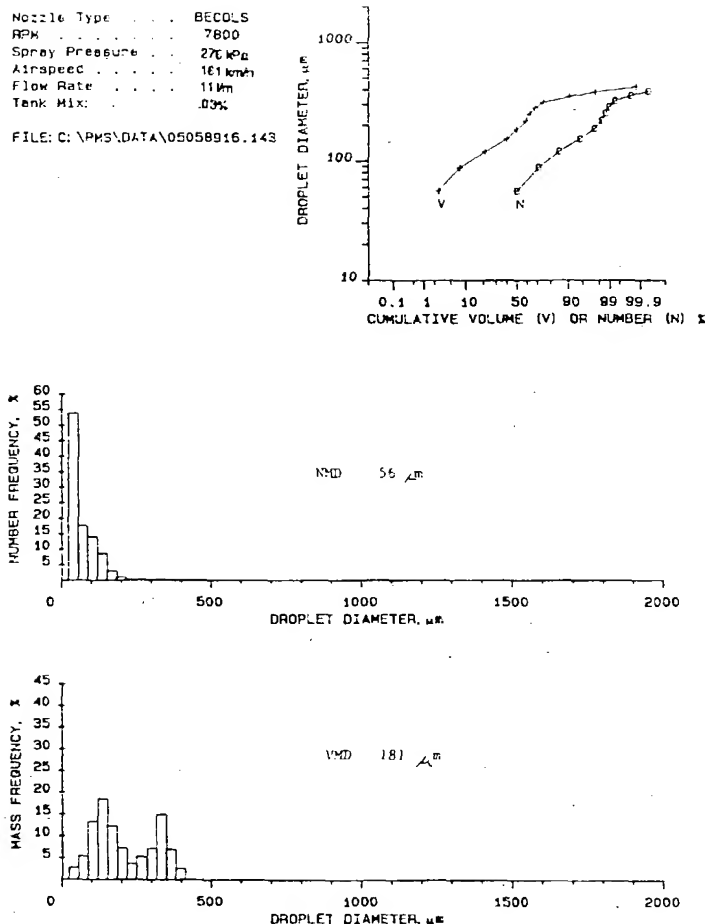


FIGURE 6. Beecomist rotary screen, 161-km/h airspeed, 12 l/min flow rate of water, plus 0.03% surfactant.

operated at 161 km/hr using an 8004 fan nozzle at 726 kPa pressure. Two sets of curves are shown. The solid lines are for the water-base mix at 90 and 135° to the airstream, showing a slight negative effect from an increase of viscosity from 0.5 to 3 mPa · s. However, the oil-based formulation shows a positive effect, increasing the drop size as viscosity is increased. Other observers have tested various formulations with results of a similar nature.<sup>6,9,13</sup>

The data graphed in Figure 12\* show the effects of peripheral screen surface velocity vs. drop size for water and for the CSO-solvent mix. The CSO mix has a much reduced surface tension (Table 1), which lowers the drop size from that of water. The peripheral velocity (related to revolutions per minute) is the dominant physical characteristic of the rotary devices controlling the drop size.<sup>7</sup>

Figure 13 indicates the effect of flow rate on rotary screen atomization. Here, a small, high-speed multiblade atomizer rotating at speeds of 22,500 to 9,300 rpm indicates that drop size increases when the flow rate is increased, primarily because the rotational speed is

\* From Akesson, N. B. and Gibbs, R. E., Pesticide drop size as a function of spray atomizers and liquid formulations, in *Pesticide Formulations and Application Systems*, Vol. 10, Bode, L. E., Hazen, J. L., and Chasin, D. G., Eds., American Society for Testing and Materials, Philadelphia, 1990, 170. With permission.

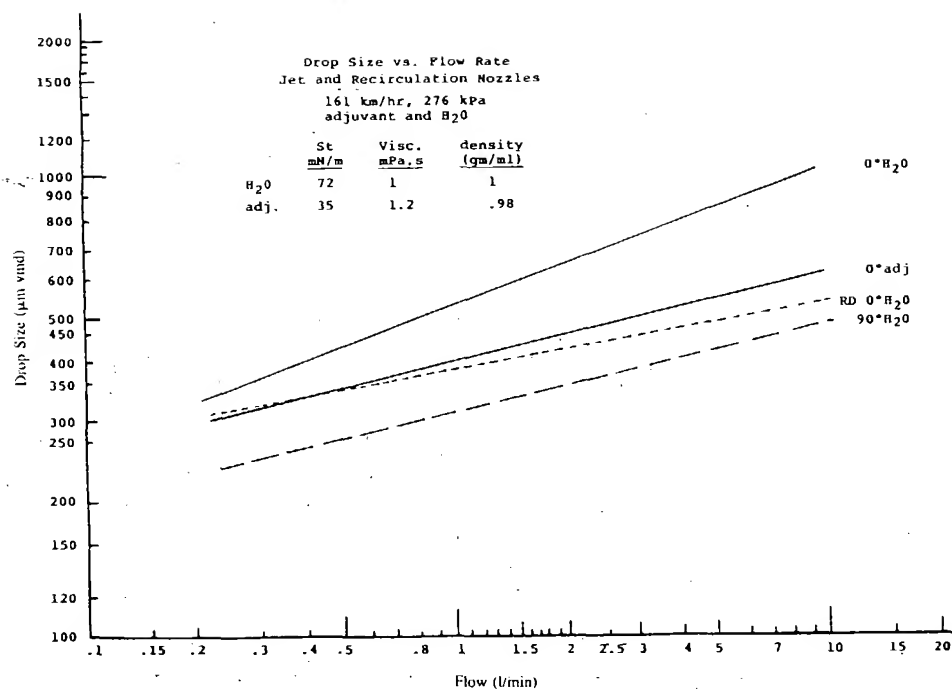


FIGURE 7. Drop size vs. flow rate for jet or orifice nozzles.\*

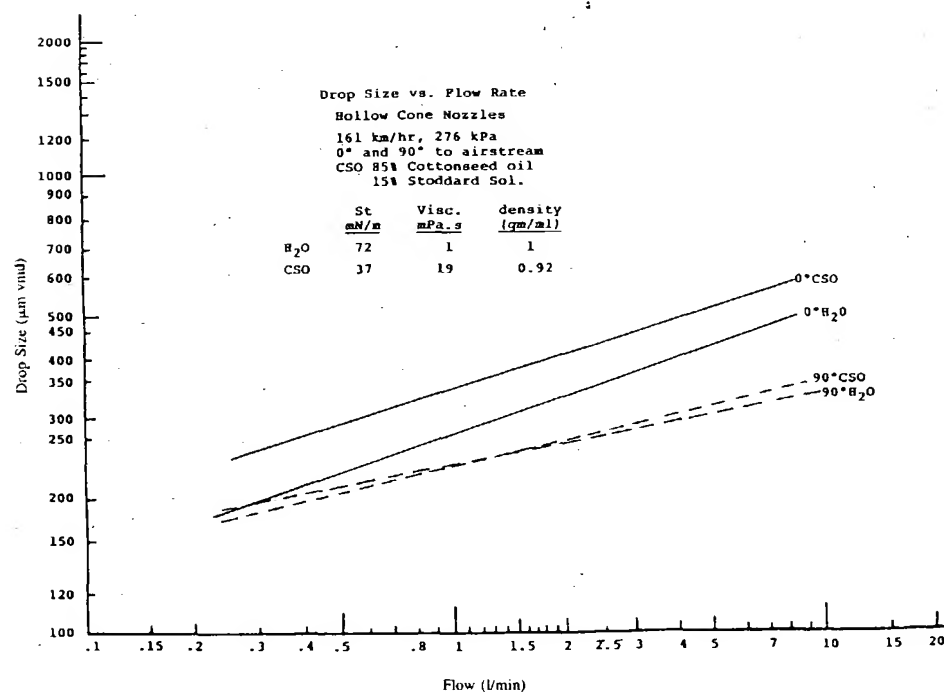


FIGURE 8. Hollow-cone nozzles, 161 km/h airspeed, 276 kPa pressure.\*

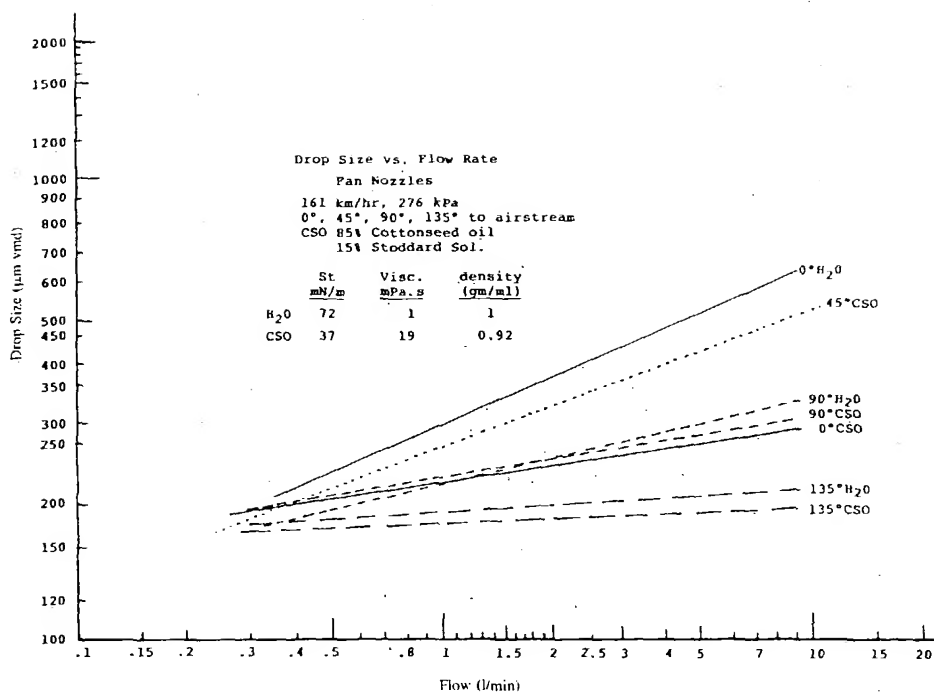


FIGURE 9. Fan nozzles, 161 km/h airspeed, 276 kPa.\*

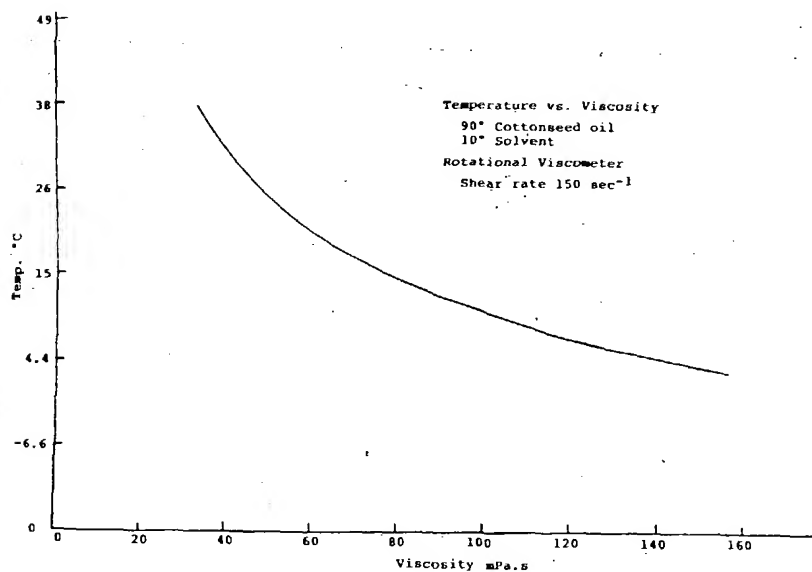


FIGURE 10. Viscosity vs. temperature for CSO-solvent mixture.

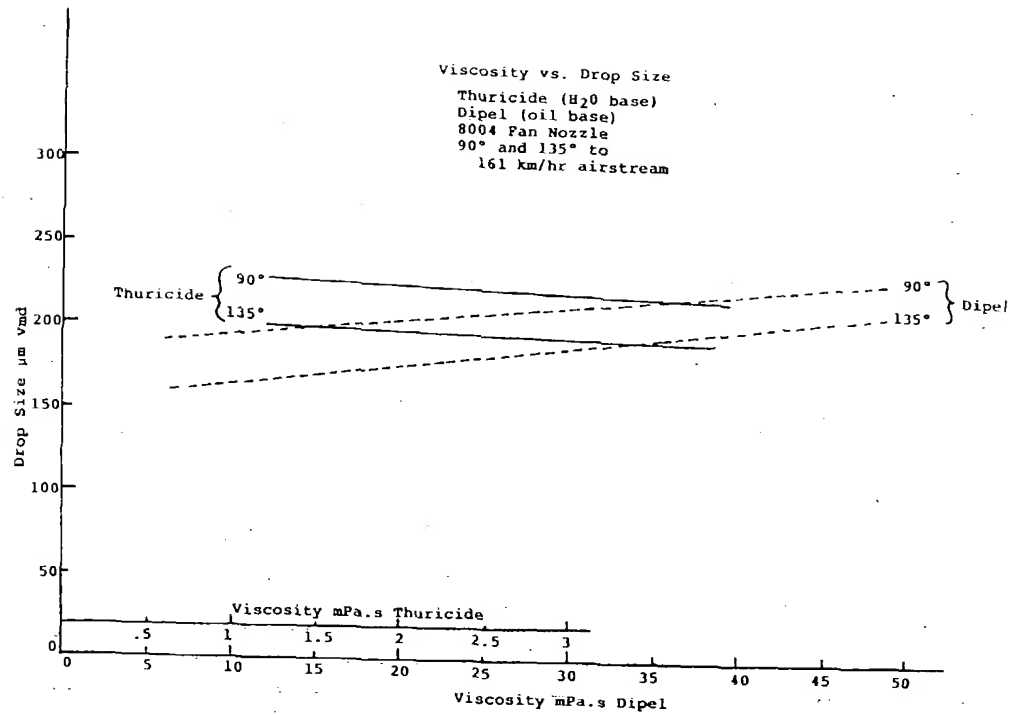


FIGURE 11. Viscosity vs. drop size for two *Bacillus thuringiensis* formulations.\*

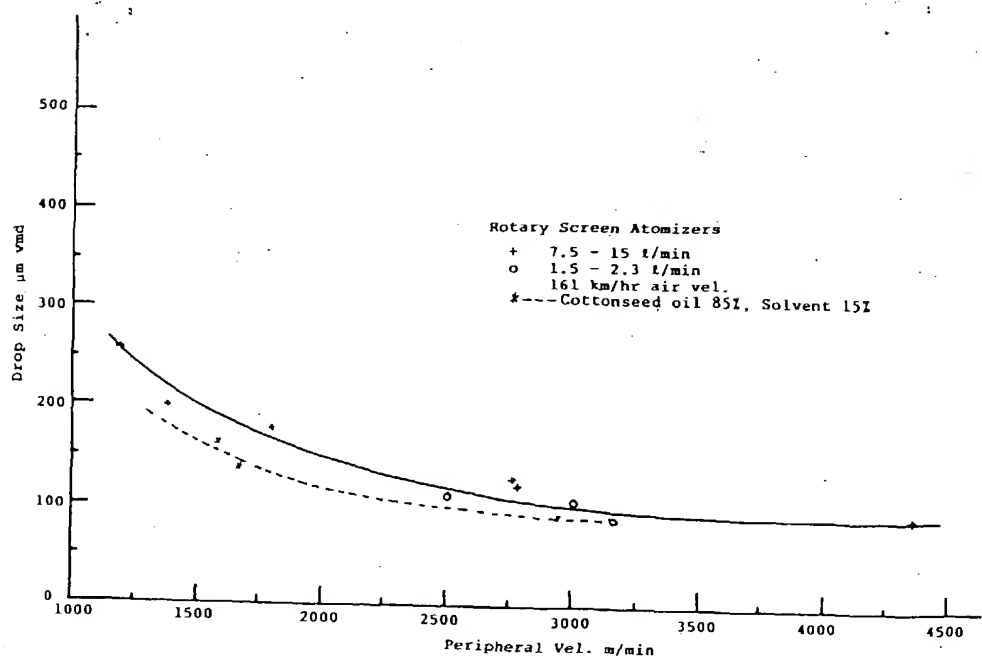


FIGURE 12. Rotary screen peripheral velocity vs. drop size for water and CSO mix.\*



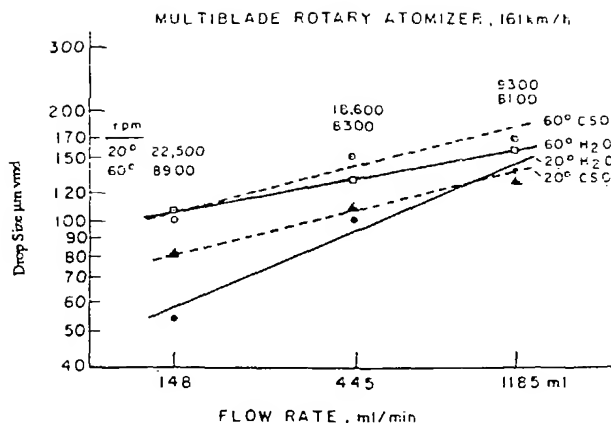


FIGURE 13. Drop size vs. flow rate rotary screen atomizer, water, and CSO.

reduced. Again, the reduced surface tension of the CSO mix indicates that smaller drop sizes are produced. The blade angles were 20 and 60°; the flatter 20° blades spun the screens at a higher rate with the same air speed of 161 km/hr.

Figure 14\* shows the results of a series of tests run with a water-soluble polymer with two hydraulic pressure nozzles, 32-mm orifice, #46 core (D8-46), and a fan type 8006. The curves show the effect of adding the viscoelastic material (in g/378 l of water) vs. the drop size in vmd. The vmd is also the  $D_{v,5}$  or 50% mode, while  $D_{v,9}$  indicates the size range at the 90% level and  $D_{v,1}$  the size range at the 10% level by volume. Thus,  $D_{v,9}$  indicates what is happening to the amount of spray volume in larger drops, while  $D_{v,1}$  is for the small-drop spectrum.

For the hollow-cone nozzle (D8-46), the larger spray drops are greatly increased as the polymer is increased, while for the D8-46  $D_{v,1}$  or small end of the range, the increase is more modest. The fan nozzle  $D_{v,9}$  shows a significant increase in large-drop mass, but it is significant to note that the small-end  $D_{v,1}$  for the fan nozzle remained the same even as the polymer was increased.

The significance here is that while adding the polymer increases the large-drop portion of the spray, it has a negligible effect on reducing small-drop production, or that portion of most concern with drift losses from spray applications.

#### IV. SUMMARY

The use of most adjuvants is aimed at enhancing, controlling, or otherwise affecting the biological response of the intended target to a given pesticide. However, along with the intended biological response is a frequently overlooked co-function which affects one of the initial characteristics of the application, that of the drop size produced. Formulation physical changes of surface tension, viscosity, density, evaporation rate (vapor pressure), and viscoelasticity may have a significant effect on the overall effectiveness of the application in a manner quite unexpected by the applicator.

Most tank-mix formulations will have a surface tension significantly less than that of water. This can also reduce the drop size of any given atomizer quite significantly, depending on other characteristics, including the angle of discharge of the spray to an airstream.

\* From Akesson, N. B. and Gibbs, R. E., Pesticide drop size as a function of spray atomizers and liquid formulations, in *Pesticide Formulations and Application Systems*, Vol. 10, Bode, L. E., Hazen, J. L., and Chasin, D. G., Eds., American Society for Testing and Materials, Philadelphia, 1990, 170. With permission.

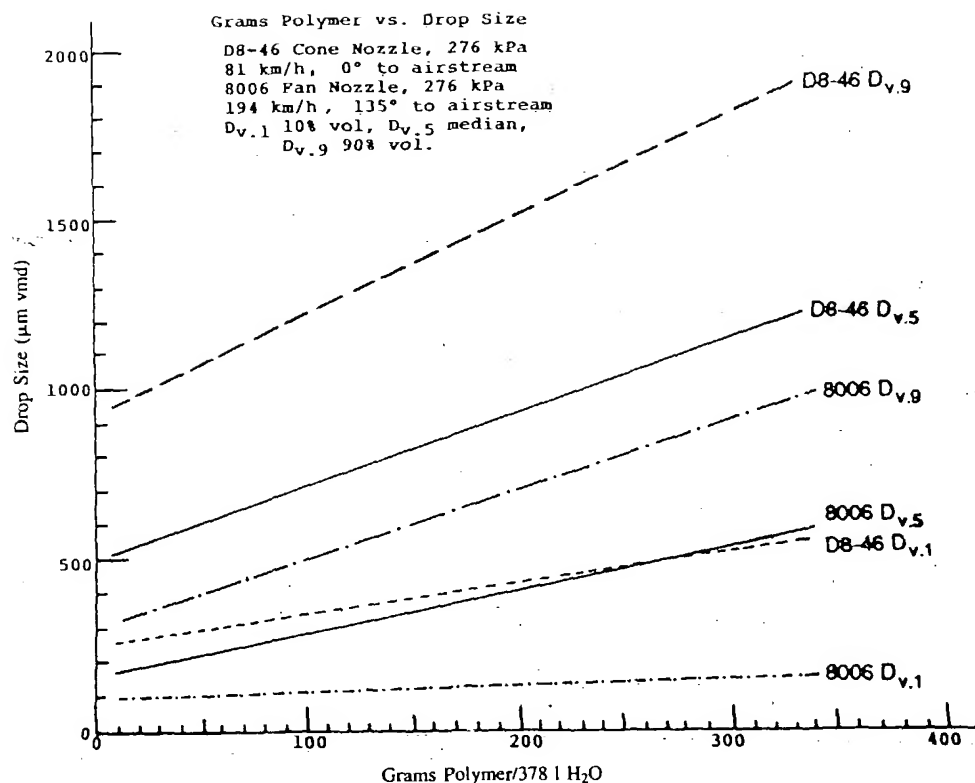


FIGURE 14. Drop size and viscoelasticity.\*

Viscosity is most noticeable because it affects the flow characteristics of the mix. Its effect on spray atomization is complex, but generally not significant. Viscoelasticity is quite separate from viscosity in its effect. For example, water-soluble polymers increase the mass of large drops, but have little effect on the mass of small drops, neither of which was a response to the liquid viscosity. Increasing the density of the mix increases the mass flow rate of a given volume of material and, hence, can affect the drop size, but only when a significant density increase is present. Vapor pressure and evaporation (interrelated) can also affect the drop size as, for example, when the increased evaporation rate reduces the drop size in the air before they contact the target. This may be good or bad, depending on the desired response to a specific application.

Overall, the physical parameters of the spray mix may add to or distract from a given application. Formulators generally are aware of these properties of their product, but users in the field are in need of better information from the producers to enable more effective and safe use of pesticides.

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## Chapter 29

**THE INFLUENCE OF ADJUVANTS ON THE PERFORMANCE OF  
A GLYPHOSATE/2,4-D MIXTURE**

Joseph H. Combellack, A. McShane, and Robert G. Richardson

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## ABSTRACT

A fluorescent tracer technique was used to measure the amount of a commercial mixture of the herbicides 2,4-D isopropylamine ( $200 \text{ g l}^{-1}$ ), glyphosate isopropylamine ( $100 \text{ g l}^{-1}$ ), and a nonionic surfactant ( $81 \text{ g l}^{-1}$ ), with and without additional surfactants, retained on leaves of subterranean clover (*Trifolium subterraneum*), radish (*Raphanus sativus* c.v. Fireball), and ryegrass (*Lolium rigidum*). Ryegrass retained more spray solution than did radish or subterranean clover. An examination of the effect of adding surfactants to the 2,4-D/glyphosate mixture showed that added surfactant reduced the amount of spray solution retained on radish and Wimmera ryegrass. Of the adjuvants tested, the cationic surfactant Ethokem produced the worst retention on the three plant species tested. Retention was reduced by 18% on subterranean clover, 44% on radish, and 30% on ryegrass. This change in retention was not reflected in changes in the dry weights of the treated species. The results are discussed in relation to changes in leaf morphology, orientation, and to the droplet spectra produced.

## I. INTRODUCTION

Chemical weed control plays a major role in contributing to the efficiency of modern farming systems. Adjuvants are present in most herbicide formulations, and their importance to agriculture parallels that of herbicides. Accurate estimates of adjuvant usage with herbicides are not published, but annual world-wide usage by 1980 probably exceeded 10 million kg (5% of the herbicide tonnage) and amounted to approximately 5% of total weed control cost.<sup>6</sup>

In recent years, there has been a proliferation in adjuvants available for addition to the spray mixture. This reflects the farmer's desire to cut chemical costs either by improving the efficiency of the spraying operation or enhancing the performance of the active ingredient or both.

All adjuvants influence one or more of the five phases of herbicide spray application proposed by Combellack.<sup>3</sup>

1. Addition of a herbicide to a diluent to make a spray solution or suspension
2. Droplet production and distribution over the target area
3. Movement of the droplets to the target
4. Impingement and retention of the droplets and their resultant effectiveness on the target
5. Achievement of a biological requirement/result

Determination of the effect of surfactants in all these phases is beyond the scope of this chapter. The experimental work reported here examines the effect of surfactants on spray deposition and the resultant effectiveness of the deposit on the target.

## II. MATERIALS AND METHODS

### A. MATERIALS

The commercial herbicide formulation used was Tillmaster® ( $200 \text{ g l}^{-1}$  2,4-D isopropylamine salt;  $100 \text{ g l}^{-1}$  glyphosate isopropylamine salt;  $81 \text{ g l}^{-1}$  MON 0818 (nonionic surfactant)).

The adjuvants used are listed in Table 1. Some of the cationic surfactants listed are thought to be repackages of the same active ingredient. All spray solutions had 0.01% (w/v) sodium fluorescein added as a water-soluble tracer.



TABLE 1  
Adjuvants Used

Trade name	Active ingredient	Type of adjuvant*	Manufacturer
NPX Agro	Formulated weak surfactants	C	Akzo Chemie, Amersfoort, Holland
Hyspray	80% (w/v) ethoxylated (15) tallow amine	C	Fine Agro Chemicals, Tenbury-Wells, Worcestershire, U.K.
Nuspray 800	80% (w/v) polyethoxylated tallow amine	C	Nufarm Chemicals P/L, Laver-ton North, Australia
Meteor	80% (w/v) tallow amine ethoxylate	C	Unknown
Ethokem	87% (w/v) ethoxylated (15) tallow amine	C	Midkem Ltd., Northampton, England
Tensio Bio-Act	Formulated weak cationic surfactants	C	C.I.K. (Aust) P/L, Perth, W.A., Australia
Agral	Alkyl phenol ethoxylate	N	I.C.I. Plant Protection, Brack-nell, U.K.
Mon 0818	Nonyl phenol ethoxylate	N	Monsanto, Leicester, U.K.
LJ 700	Phosphatidyl choline	Activator adjuvant	Loveland Industries Inc., Colo-rado, U.S.A.
DC-Tron	Highly refined petroleum oil	Oil	Ampol, Brisbane, Australia
Nu-film 17	Di-1- <i>p</i> -menthene	Sticker spreader	Meller Chemical Corp., Penn-sylvania, U.S.A.

\* C, cationic surfactant; N, nonionic surfactant.

## B. EFFECT OF ADJUVANTS ON DROPLET SPECTRA

The effect of the adjuvants on spray droplet size was measured using a Malvern Instruments Particle Size Analyser Type ST 1800 (Malvern Instruments, Spring Lane, Malvern, Worcestershire, U.K.). Tests were carried out using a single-orifice brass flat-fan nozzle SS110015 (Spraying Systems Inc., Wheaton, IL). An operating pressure of 300 kPa was used which was measured by a pressure gauge fitted as close to the nozzle as possible. The nozzle was mounted 7.5 cm from the laser beam and droplet spectra measurements were made laterally, through the long axis of the spray fan, using a 600-mm lens.<sup>1</sup>

## C. PLANT MATERIALS

Seeds of Wimmera ryegrass, radish, and subterranean clover were sown in a commercial peat moss and nutrient mixture, Jiffy 7® (Jiffy Research and Service, Oslo, Norway), and germinated in a shade house. After emergence, the ryegrass was thinned to three seedlings per pot, subterranean clover to two, and radish to one. The plants were sprayed 21 d after planting.

## D. SPRAY APPLICATION DETAILS

The spray was applied using two brass Spraying Systems flat fan 110015 nozzles 50 cm apart on a boom 45 cm above the plant canopy. At an operating pressure of 300 kPa, each nozzle delivered 640 ml min<sup>-1</sup>, which at an operating speed of 12 km hr<sup>-1</sup> gave an application volume of 60 l ha<sup>-1</sup>.

## E. ASSESSMENTS OF SPRAY RETENTION

For each plant sample, the leaves were washed with 0.005 M sodium hydroxide solution to remove the fluorescein. The fluorescein concentration was measured using a Pye Unicam Spectrophotometer with a fluorimeter attachment. The leaf areas were measured using a

TABLE 2  
Effect of Adjuvants on Droplet Spectra

Spray solution (v/v)	% of droplets by volume*		
	<100 $\mu\text{m}$	100 to 300 $\mu\text{m}$	>300 $\mu\text{m}$
3.3% Tillmaster	30.7 a	60.2 abc	09.1 a
+ 0.5% Nu-film 17	27.7 b	60.7 bc	11.6 b
+ 0.5% Ethokem	29.9 a	59.6 ab	10.5 ab
+ 0.5% Nuspray 800	30.8 a	59.3 ab	09.9 ab
+ 0.5% Agral	29.5 ab	59.7 abc	10.8 ab
+ 0.5% Hyspray	30.9 a	58.7 a	10.4 ab
+ 0.5% Meteor	30.0 a	59.3 ab	10.7 ab
+ 0.5% NPX Agro	30.8 a	58.4 a	10.8 ab
0.1% Agral only	19.8 c	60.2 ab	18.9 c
H <sub>2</sub> O only	17.1 d	61.5 c	21.4 d
SEM			
Error d.f.	33.0	33.0	33.0
Total d.f.	43.0	43.0	43.0
C. of V. (%)	0.48	01.9	11.6

\* Any two means having a common letter are not significantly different at the 5% level; C. of V., coefficient of variation.

planimeter. This enabled the volume of spray retained per unit area of leaf surface to be calculated. Statistical analysis was carried out using this figure.

#### F. EFFECT OF ADJUVANTS ON RETENTION

To assess this effect on spray retention and the subsequent performance of the herbicide Tillmaster, the adjuvants listed in Table 1 were tested at a concentration of 0.5% (v/v) in the spray mixture, over two separate spraying sessions. Tillmaster was used at a rate equivalent to  $2 \text{ l h}^{-1}$  in an application volume of  $60 \text{ l ha}^{-1}$ . In each experiment, spray retention was measured on radish, ryegrass, and subterranean clover, but the biological effect of additives when added to Tillmaster was only assessed against subterranean clover and ryegrass, as the radish was mostly killed.

#### G. EXPERIMENTAL DESIGN AND ANALYSIS

Retention studies used a minimum of six replicates for each of the three plant species used. Three pots of each species were randomly removed to form one replicate for spray retention analysis, and the remaining three pots of each species were returned to the shade-house. These pots formed one replicate for dry weight analysis by cutting the plant to soil level after 21 d and placing it in an oven at  $85^\circ\text{C}$  for 48 h and then weighing. The subsequent dry weight measurements were used to assess the biological performance of the spray solution using analysis of variance.

### III. RESULTS

#### A. EFFECT OF ADDING ADJUVANTS TO TILLMASTER ON DROPLET SPECTRA

The results presented in Table 2 show that, of all the adjuvants, only the addition of 0.5% Nu-film 17® significantly affected droplet spectra when compared with Tillmaster alone. This adjuvant significantly increased the droplets over  $300 \mu\text{m}$  and reduced those

TABLE 3  
Effect of Rate on Tillmaster on Retention by Ryegrass

Tillmaster (l ha <sup>-1</sup> )	Tillmaster measured (μl cm <sup>-2</sup> )	Tillmaster calculated (μg a.i. cm <sup>-2</sup> ) <sup>a</sup>	Expected collection (μg a.i. cm <sup>-2</sup> ) <sup>b</sup>	Dry weight (g) sprayed plants 21 DAT <sup>c</sup>
0.125	0.589	00.368	01.011	635
0.250	0.571	00.714	02.023	463
0.500	0.906	02.225	04.045	372
2.000	1.618	16.180	16.180	320
4.000	1.654	33.080	32.360	274

<sup>a</sup> Calculated using the formula:  $\text{Herbicide} \frac{\text{g a.i. l}^{-1} \times \text{dose rate l ha}^{-1}}{\text{vol. of application l ha}^{-1} \times 10^6} \times \mu\text{l cm}^{-2}$

<sup>b</sup> Based on that measured for normal dose rate of Tillmaster, i.e., 2 l ha<sup>-1</sup>.

<sup>c</sup> Days after treatment.

TABLE 4  
Effect of Rate of Tillmaster on Retention by Subterranean Clover

Tillmaster (l ha <sup>-1</sup> )	Tillmaster measured (μl cm <sup>-2</sup> )	Tillmaster calculated (μg a.i. cm <sup>-2</sup> ) <sup>a</sup>	Expected collection (μg a.i. cm <sup>-2</sup> ) <sup>b</sup>	Dry weight (g) sprayed plants 21 DAT <sup>c</sup>
0.125	0.177	00.111	00.428	520
0.250	0.174	00.218	00.856	322
0.500	0.699	01.748	01.713	338
2.000	0.688	06.850	06.850	176
4.000	0.880	17.600	13.700	179

<sup>a</sup> Calculated using the formula:  $\text{Herbicide} \frac{\text{g a.i. l}^{-1} \times \text{dose rate l ha}^{-1}}{\text{Vol. of application l ha}^{-1} \times 10^6} \times \mu\text{l cm}^{-2}$

<sup>b</sup> Based on that measured for normal dose rate of Tillmaster, i.e., 2 l ha<sup>-1</sup>.

<sup>c</sup> Days after treatment.

less than 100 μm in diameter. The results also show that the spectra are significantly changed by Tillmaster with or without other adjuvants when compared to water, as droplets over 300 μm were significantly reduced, while those under 100 μm were significantly increased.

#### B. EFFECT OF TILLMASTER DOSE ON RETENTION AND EFFICACY

The results in Tables 3 and 4 show that the amount of spray retained varied with dose rate. As the fluorescein was dissolved in the diluent, similar retention was expected at each dose rate. However, retention at the 0.125 and 0.250 l ha<sup>-1</sup> dose rates was approximately one fourth that expected. Thus, the amount of active ingredient collected was also affected.

#### C. EFFECT OF ADJUVANTS ON RETENTION AND EFFICACY OF TILLMASTER

Tables 5 and 6 demonstrate that in some cases, addition of adjuvant significantly reduces retention when compared with Tillmaster alone. However, this was not reflected in the corresponding biological effect. None of the adjuvants improved retention, while two in particular, the cationic tallow amines Nuspray 800® and Meteor®, significantly reduced collection on the three test plant species. As the reduction in retention was not reflected in a reduced biological effect, there must be a positive effect from the adjuvant.

TABLE 5  
Effect of Additives on the Retention and Biological Performance of  
Tillmaster

Treatment <sup>a</sup>	Subterranean clover		Ryegrass		Radish retention <sup>b</sup> ( $\mu\text{l cm}^{-2}$ )
	Retention ( $\mu\text{l cm}^{-2}$ )	Dry weight	Retention ( $\mu\text{l cm}^{-2}$ )	Dry weight	
Tillmaster only	2.438 a	474 ab	4.285 a	251 a	2.539 a
+ 0.5% Nu-film 17 (SS)	2.374 a	599 bc	3.459 ab	231 a	2.432 a
+ 0.5% Agral (N)	2.416 a	503 ab	3.247 ab	268 a	2.024 b
+ 0.5% Hyspray (C)	2.233 a	433 ab	3.294 ab	318 a	1.553 c
+ 0.5% Ethokem (C)	1.991 a	418 a	2.991 bc	299 a	1.416 c
Water only	1.145 b	678 c	2.105 c	477 b	1.202 d
SEM	0.278	72	0.494	57	0.103
Error d.f.	25	25	25	25	25
Total d.f.	35	35	35	35	35
C. of V. (%)	22.9	24.1	26.5	31.9	29.8

Note: Any two means having a common letter are not significantly different at the 5% level of significance.

<sup>a</sup> SS, spreader sticker; N, nonionic; C, cationic; C. of V., coefficient of variation.

<sup>b</sup> No dry weight for radish, as all plants were killed.

TABLE 6  
Effect of Additives on the Biological Performance of Tillmaster

Treatment <sup>a</sup>	Subterranean clover		Ryegrass		Radish retention <sup>b</sup> ( $\mu\text{l cm}^{-1}$ )
	Retention ( $\mu\text{l cm}^{-2}$ )	Dry weight	Retention ( $\mu\text{l cm}^{-2}$ )	Dry weight	
Tillmaster only (3.3%)	2.426 a	794	4.961 a	738 a	2.545 a
+ 0.5% DC-Tron (oil)	2.153 ab	762	3.346 b	733 a	2.128 b
+ 0.5% LI 700 (activator)	2.079 ab	810	3.968 b	664 a	2.086 b
+ 0.5% Tension Bio-Act (C)	1.995 ab	742	2.276 cd	646 a	1.945 bc
+ 0.5% NPX Agro (C)	1.730 bc	672	2.627 bc	673 a	1.886 bc
+ 0.5% Nuspray 800 (C)	1.709 bc	632	2.148 d	707 a	1.732 bcd
+ 0.5% Meteor (C)	1.50 c	835	2.160 d	658 a	1.585 cd
H <sub>2</sub> O only	0.927 d	882	1.417 d	1068 b	1.417 d
SEM	0.20	94	0.172	70	0.201
Error d.f.	35	35	35	35	35
Total d.f.	47	47	47	47	47
C. of V (%)	19.1	21.3	24.2	16.5	18.2

Note: Any two means having a common letter are not significantly different at the 5% level of significance. No letters in a column indicate no significant differences between any treatments in that column.

<sup>a</sup> C, cationic.

<sup>b</sup> No dry weights for radish, as all plants were killed.

#### IV. DISCUSSION

The droplet spectra results showed that the addition of adjuvant to water changes the droplet spectra measured. In particular, in these tests, the small droplet component ( $<100 \mu\text{m}$ ) was increased, whereas those over  $300 \mu\text{m}$  were decreased. This is contrary to the



findings of Combellack and Matthews,<sup>2</sup> Dempsey et al.,<sup>4</sup> and Wynen and Combellack,<sup>7</sup> who reported a decrease in the small-droplet component, although it agrees with the results of Moerkerk and Combellack.<sup>5</sup> The reason for this difference could reflect differences in the nozzle used or inherent physical characteristics of the Tillmaster formulation. The increase in the small-droplet component could result in an increase in droplet drift and in the number of droplets per unit volume. The latter effect would result in the possibility of increased droplet density per unit area on the target. It would also result in a greater number of droplets arriving at the target with lower terminal velocities, thus possibly explaining in part the changes in retention efficiency. Furthermore, as the results show that the addition of adjuvant to Tillmaster did not change the droplet spectra, it can be rationalized that differences in collection, when compared with that between water and Tillmaster, must reflect other factors.

By grouping the spray retention data for the addition of adjuvants, it can be seen that the cationic materials, mainly tallow amines, markedly decrease retention compared with the other materials tested. Furthermore, by grouping the bioactivity data, it can be seen that the addition of the cationic materials generally has a more positive effect on reducing the dry weight of subterranean clover 21 d after treatment, while it is negative on ryegrass. Therefore, although the addition of cationic materials reduces retention, this is not always reflected in a similar effect on biological activity. The Tillmaster formulation consistently provided the best retention and almost always the optimum biological activity. Thus, the addition of adjuvants to Tillmaster is not cost effective.

The results show that the retention of Tillmaster changes with concentration, and the effect is influenced by the level of surfactants. When their concentration is less than 0.4% (w/v), retention is substantially less; however, when above this concentration, it remains relatively constant. This indicates that the concentration of adjuvant must be above the critical micelle level if a relationship between additional adjuvant on retention and bioactivity is to be measured.

It can be concluded from the data that there are differences in the retention efficiency between weedy species. The addition of adjuvants to recommended spray mixtures may be deleterious to retention and efficacy. Droplet spectra will be changed, which appears to improve retention, but not necessarily biological activity. Cationic surfactants appear to improve the biological activity of the herbicide Tillmaster on subterranean clover, but has a negative effect on ryegrass.

## ACKNOWLEDGMENT

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## Chapter 30

**THE RELATIONSHIP BETWEEN SPRAY RETENTION AND  
HERBICIDAL EFFICACY OF DICLOFOP-METHYL**

Michael R. Moerkerk and Joseph H. Combellack

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## ABSTRACT

The effects of selected adjuvants, an emulsifiable oil and two nonionic surfactants on spray retention and subsequent biological performance of the postemergent grass herbicide, diclofop-methyl (as Hoegrass®, Hoechst Australia Ltd., Melbourne, Australia, 375 g of active ingredient [a.i.] per liter) were assessed on wild oat (*Avena fatua*) and Wimmera ryegrass (*Lolium rigidum*). While the three adjuvants had no significant effect on spray collection on wild oat, it was increased with increasing rates of diclofop-methyl. The average retention of Wimmera ryegrass was over 50% more than that observed on wild oat. However, on Wimmera ryegrass, neither herbicide rate nor adjuvant influenced retention. The potency of the herbicide was enhanced by the emulsifiable oil, on both wild oat and Wimmera ryegrass, while the nonionic surfactants were somewhat antagonistic. Spray retention on wheat cultivars followed the same pattern of retention as observed on wild oat. No effect on dry weights of the wheat cultivars was observed with or without the emulsifiable oil. The results indicate that the effects of adjuvants on spray retention cannot adequately predict their effects on herbicide potency. Diclofop-methyl alone has a greater influence on spray retention than adjuvants and it behaves differently on different plant species. As there appears to be no correlation between adjuvant effect on spray retention and herbicidal potency, adjuvant activity must be related to other processes.

## I. INTRODUCTION

Frequently, herbicide or adjuvant manufacturers recommend the addition of adjuvants to spray mixes to enhance herbicide performance. It is believed that the majority of adjuvants modify the spray mix to improve coverage and retention under adverse conditions. For example, increased spray collection has been observed on wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), and wild oats when an emulsifiable petroleum oil was added to diclofop-methyl.<sup>3</sup> Also, Streibig and Thonke<sup>5</sup> reported an improvement in alloxym-sodium and sethoxydim potency with increasing adjuvant concentration.

Adjuvants affect spray retention in other ways. For example, spray retention has also been changed by varying the concentration of herbicide 2,4-D on wheat, Wimmera ryegrass, and radish (*Raphanus sativus*).<sup>2</sup> The latter authors also found that as the concentration of 2,4-D amine was increased, consistent increases in spray retention on wheat and ryegrass were observed regardless of the three nozzle types used, but with 2,4-D ester formulation, it was only increased with one type of nozzle. Retention of spray by radish and ryegrass was not consistently affected by concentration.

It can thus be seen that the effect of an adjuvant on a herbicide's performance is not predictable. Thus, to enable accurate recommendations, it is necessary to test the herbicide, plant species, and adjuvant interactions. This is normally assessed on the basis of biological effect. As this is impractical on a time basis, the present work was undertaken to assess whether it is possible to relate changes in spray retention to herbicidal effect. It was reasoned that if such a relationship existed, then assessments could be accelerated as the studies can be more rapidly executed.

## II. MATERIALS AND METHODS

### A. MATERIALS

Trials were carried out using the postemergence herbicide diclofop-methyl (as Hoegrass containing 375 g a.i. l<sup>-1</sup>), an emulsifiable petroleum oil (BP Ulvapron®, BP Australia Ltd., Melbourne, Australia) and two nonionic surfactants (Agral 60® and Teric 12A6®, ICI Aus-

tralia Ltd., Melbourne, Australia). All the spray solutions had 0.01% (w/v) of sodium fluorescein added as a water-soluble tracer.

## B. PLANT MATERIAL

Wimmera ryegrass and wild oats were chosen as they are the major targets for diclofop-methyl use in Australia. Seeds of wild oats were germinated at 15°C, 24 h in the dark for 7 d. Wimmera ryegrass was germinated at 15°C for 12 h in the dark, intermittent with 25°C for 12 h in light, for 7 d.

Either two germinated seeds of wild oats or five of Wimmera ryegrass were planted in a commercial peat and nutrient mixture (Jiffy 7®, Jiffy Research and Service, Oslo, Norway) and grown in a shadehouse under ambient conditions. When plants were 28 d old (growth stages 12 to 22<sup>6</sup>), 16 pots of each species were randomly arranged in trays 34.5 × 28.0 cm to form one treatment.

## C. APPLICATION DETAILS

The plants were sprayed with a laboratory track sprayer which consisted of a mounted boom with two Spraying Systems sintered alumina flat fan 110015 nozzles 50 cm apart. The boom height above the plants was 30 cm. The velocity of the boom was 12 km hr<sup>-1</sup>. A pressure of 200 kPa gave a delivery volume of 500 ml min<sup>-1</sup> nozzle<sup>-1</sup>, giving an application volume of 50 l ha<sup>-1</sup>.

Treatments were designed to assess the effects of BP Ulvapron (2%, v/v), Agral 60 (0.06%, v/v), and Teric 12A6 (0.5%, v/v) on the spray retention and subsequent biological performance of diclofop-methyl on wild oats and Wimmera ryegrass.

## D. DROPLET SPECTRA MEASUREMENTS

Droplet spectra of the nozzles were measured for each spray solution using a Malvern 2200 particle sizer. The laser beam was passed through the long axis of the spray sheet 15 cm from the nozzle. A Spraying Systems sintered alumina 110015 nozzle was used at a pressure of 200 kPa. The data collected was fitted to a Rosin Rambler distribution model and the weight of spray in the diameter range of <100, 100 to 300, and >300 µm were calculated.

## E. SPRAY RETENTION MEASUREMENTS

A fluorescent tracer technique<sup>4</sup> was used to assess the amount of spray retained on the plant surface. After spraying, eight pots each of ryegrass and wild oat plants were harvested to ground level, placed in separate plastic bags, and shaken for 30 s with 30 ml of 0.005 M NaOH solution. The fluorescein concentration was measured in a Pye Unicam Spectrophotometer with a fluorimeter attachment and an autocell for rapid sample handling. The leaf area of each replicate was determined using a Paton Electronic Planimeter. The amount of spray retained was expressed as volume per unit leaf area.

The remaining unharvested plants were potted into 15-cm plastic pots with commercial potting mix, returned to the shadehouse, and allowed to grow for 28 d. After this time, the dry weights of the aboveground parts were determined by cutting the plants at the soil surface and drying them at 90°C for 24 h. This enabled an estimate of the efficacy of the herbicide to be determined by plotting dry weight against herbicide dose.

Seeds of wheat — cv. Condor, Matong, Merring, and Oxley — were germinated for 4 d under the same temperature and light regime used for the ryegrass. For each cultivar, ten seeds were placed in 20-cm plastic pots containing a commercial potting mix. The pots were placed in the shadehouse and grown for 28 d. Application of spray solution was performed as for the ryegrass/wild oats trial. One pot of each cultivar was sprayed as one



TABLE 1  
Droplet Spectra Data for Spraying Systems 110015 Nozzles at 200 kPa Diclofop-Methyl with and without BP Ulvapon®

Rate (l ha <sup>-1</sup> )	% of droplets by volume					
	Diclofop-methyl			+ BP Ulvapon (2%, v/v)		
	<100 $\mu$ m	100 to 300 $\mu$ m	>300 $\mu$ m	<100 $\mu$ m	100 to 300 $\mu$ m	>300 $\mu$ m
0.0	17.5	61.2	21.3			
0.1	11.3	69.2	19.5	11.7	70.0	18.3
0.2	10.3	69.3	20.4	12.2	70.4	17.4
0.4	10.5	67.9	21.6	10.5	70.8	18.7
0.8	10.5	69.0	20.5	10.6	72.8	16.6
1.6	11.6	68.9	19.5	10.8	73.1	16.1
2.0	10.6	71.5	17.9	11.7	72.6	15.7

replicate. Four replicates were used in all. Herbicide treatments consisted of diclofop-methyl at 0, 0.75, 1.0, 1.25 and 1.5 l ha<sup>-1</sup> with BP Ulvapon at 2% (v/v).

After spraying, five plants from each pot were removed by cutting at soil level. The five plants were combined and washed in 0.005 M NaOH to determine the spray collected. The cut surfaces of the plants in the pots were treated with glyphosate applied with a cotton bud to eliminate any root competition with the five remaining plants. The pots were then returned to the shadehouse and dry weights were determined 28 d later.

#### F. STATISTICS

Box Cox analysis was performed on the retention and dry weight data to determine the most appropriate transformation prior to statistical analysis. Either a log<sub>10</sub> or a square-root transformation was required. Data presented here have been back-transformed to allow easy interpretation of the results.

### III. RESULTS

#### A. DROPLET SPECTRA MEASUREMENTS

Droplet spectra measurements indicate a reduction in the proportion of droplets >300 and <100  $\mu$ m as the rate of diclofop-methyl was increased (Table 1). The adjuvants had little or no effect on the droplet spectra once Hoegrass was included in the spray solution. This indicates that the addition of adjuvants to Hoegrass will not greatly affect the droplet spectra produced.

#### B. EFFECT OF DICLOFOP-METHYL DOSE ON RETENTION

Spray retention by wild oats increased with increasing herbicide dose. Spray retention was not significantly influenced by adjuvant on either wild oats or ryegrass. Herbicide rate did not consistently alter the spray retained by ryegrass (Figure 1), but this species consistently retained more spray than either wild oats (Figure 2) or wheat (Figure 3).

#### C. EFFECT OF ADJUVANTS ON RETENTION OF DICLOFOP-METHYL ON WILD OATS AND RYEGRASS

The effectiveness of adjuvants to enhance herbicide performance can be described by fitting a dose-response curve to the data. Streibig and Thonke<sup>5</sup> used a sigmoidal model to describe the dose response. Figure 2 shows the dose-response curves for the three adjuvants on wild oats. It can be seen that the effect of BP Ulvapon is to move the curve to the left,



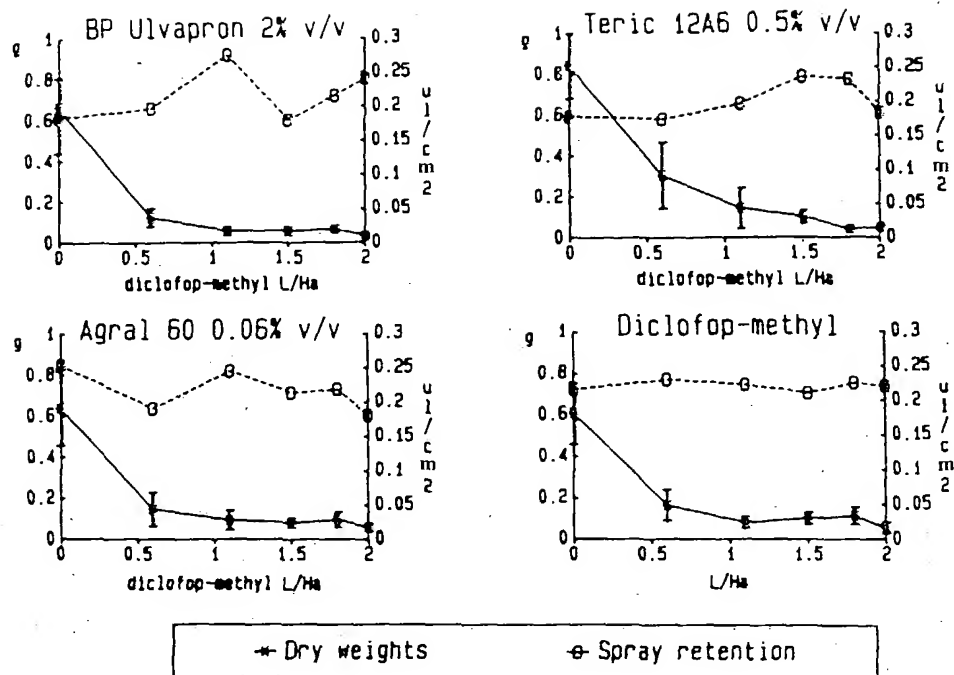


FIGURE 1. Effect of adjuvants on spray retention and subsequent biological performance of diclofop-methyl on Wimmera ryegrass.

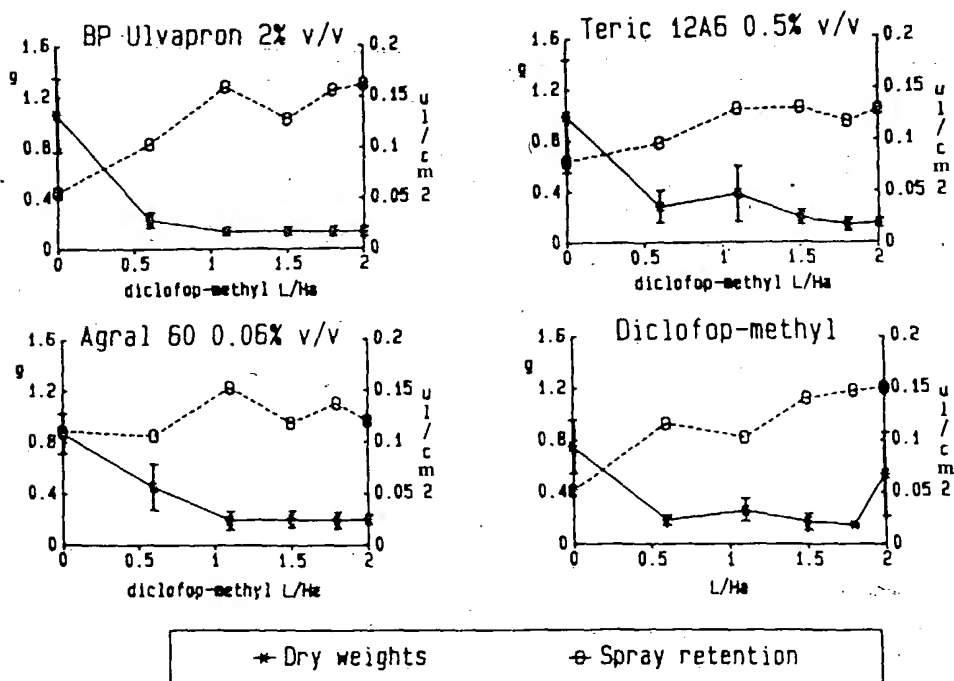


FIGURE 2. Effects of adjuvants on spray retention and subsequent biological performance of diclofop-methyl on wild oats.

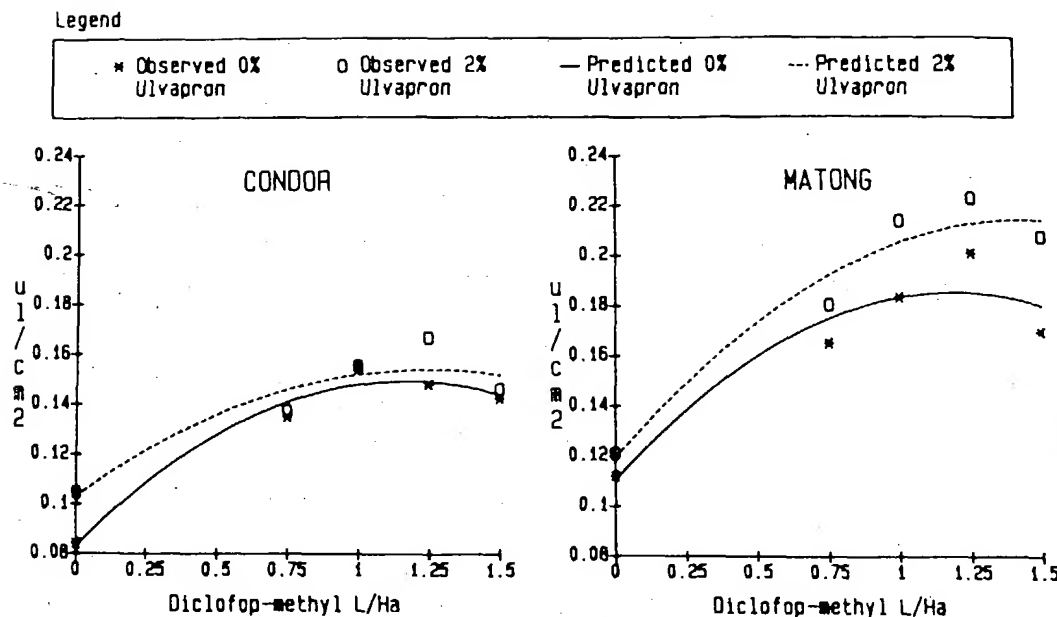


FIGURE 3. Effect of the adjuvant BP Ulvapron on spray retention on two wheat cultivars.

which indicates an increase in herbicide potency. This improvement in potency does not correlate with any improvement in spray retention. Teric 12A6 and, to a lesser extent, Agral 60 can be seen to be antagonistic to diclofop-methyl performance, as indicated by the shift in the curves to the right. The 95% confidence limits overlaying the graphs of wild oats indicate that there was less variability in dry weight response when BP Ulvapron was added to the spray mix.

The rates of diclofop-methyl were too high to be able to assess the dose-response curves observed on Wimmera ryegrass; however, the data presented in Figure 1 indicate that Teric 12A6 was antagonistic to diclofop-methyl performance, while Agral 60 and BP Ulvapron had little effect on its performance. The errors overlaying the graphs show that the variability of the response to BP Ulvapron is less than those observed with diclofop-methyl used alone. This indicates a faster kill of all the plants treated, which may reflect increased potency.

#### D. EFFECT OF DICLOFOP-METHYL DOSE RATE ON RETENTION BY WHEAT

Spray retention by wheat follows a pattern similar to that observed on wild oats. Two of the cultivars, Condor and Matong, show a declining rate of increase in retention as the herbicide rate is increased (Figure 3). A maximum level of retention is observed when the diclofop-methyl rate is  $1.25 \text{ l ha}^{-1}$ . BP Ulvapron at 2% improved spray retention on all the wheat cultivars by 1 to 30%. Analysis of the dry weights of the four cultivars did not give any indication that this increase in spray retention resulted.

### IV. DISCUSSION

The effect of adding spray to the diluent, water, was to reduce the small-droplet component. This supports previous findings.<sup>1,2</sup> By decreasing the small-droplet component, the drift potential is decreased. The results also indicate that adding adjuvant to a diclofop-methyl spray mixture will not greatly affect the droplet spectra.

The greater spray retention per unit area by Wimmera ryegrass compared with wild oats may explain in part the difference in the herbicide susceptibility of these species to diclofop-methyl. The increased retention of more than 50% observed here supports the findings of Combellack and Richardson,<sup>1</sup> who found that Wimmera ryegrass consistently retained between three and ten times more spray than wheat. These differences may be related to the plants' structure. Ryegrass, being tall and thin, may be better to intercept and retain the smaller droplet component of the spray than the wider, broader, flatter leaves of wheat and wild oats.

The results supported previous findings of Richardson and Combellack<sup>1</sup> in demonstrating substantial differences in retention between varieties of wheat. Furthermore, this effect was exacerbated by the addition of the adjuvant BP Ulvapon.

In conclusion, these results show that the sprays tested would decrease the droplet drift hazard compared with water. While spray retention is changed when adjuvant is added to the spray, this was not reflected by biological effect. Also, spray retention was not able to be related to efficacy. Therefore, to assess the effect of an adjuvant-herbicide-plant species interaction, it will be necessary to do biological assessments and/or conduct other physical measurements for the spray solution, to determine whether any relationship exists.

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## Chapter 31

**THE EFFECT OF ADJUVANTS ON THE LOCATION OF  
HERBICIDE DEPOSITS ON WILD OATS**

Paul Wynen and Joseph H. Combellack

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## ABSTRACT

Studies were initiated to assess whether the addition of selected adjuvants alter the location of herbicide deposits on plants, and to determine if any such changes could be correlated with biological effect. The postemergent grass-killing herbicides, diclofop-methyl as Hoegrass containing 375 g of active ingredient (a.i.) per liter (at rates of 0.05 to 1.6 l ha<sup>-1</sup>) and flamprop-methyl as Mataven containing 375 g a.i. l<sup>-1</sup> (at rates of 1.0 to 16.0 l ha<sup>-1</sup>) were applied with and without a nonionic surfactant and an emulsifiable oil to wild oat (*Avena fatua* L.). A fluorometric technique used to measure spray retention showed that with diclofop-methyl, retention by the top and middle of the plant was similar but lower than that of the basal part of the plant. With flamprop-methyl, retention by the top of the plant was higher than that of the middle, which in turn retained more than the basal area of the plant. While the addition of adjuvant decreased the amount of diclofop-methyl retained on the basal area and increased the amount retained on the top of the plant, with flamprop-methyl, it did not make any appreciable change. Diclofop-methyl potency was improved by 10 to 15% with a nonionic surfactant and by 40 to 50% with an emulsifiable oil. With flamprop-methyl, the addition of adjuvant had a nonsignificant variable effect. The results confirm other work indicating that there is no correlation between total spray retention and efficacy. Furthermore, they show that the location of the spray retention is different for the two herbicides evaluated.

## I. INTRODUCTION

There is an increasing need to reduce herbicide dose rates as a consequence of a growing demand for a contaminant-free environment. One method which has the potential to reduce dose rates is the use of spray adjuvants.<sup>12,14</sup> Adjuvants are present in most commercial formulations,<sup>7,12,14</sup> but a growing body of research has revealed that in many cases, herbicide dose rates can be reduced by the addition of further adjuvants to the commercially formulated herbicides.<sup>12,14</sup> However, their mode of action is still poorly understood. Recent work by Moerkerk et al.<sup>9</sup> revealed that while adjuvants enhanced herbicidal efficacy, this was not correlated with increased spray retention. Furthermore, the location at which a herbicide is retained on a plant influences herbicidal efficacy.<sup>5,10</sup>

One objective of this work was to determine whether adjuvants alter the spray location of plants. The second was to assess whether spray retention was affected by adjuvants. The third aimed to assess whether biological effect could be related to spray retention or to the location of the spray on the plant.

Two postemergent herbicides, diclofop-methyl and flamprop-methyl, were tested with or without the adjuvants Howet (nonionic surfactant containing 776 g l<sup>-1</sup> isotridecanol polyglycol ether) and Ulvapon (emulsifiable oil containing 92%, v/v, 150N isoparaffinic oil + 3%, v/v, mixed emulsifiers).

## II. MATERIALS AND METHODS

### A. PLANT MATERIAL

Wild oat seeds were pregerminated and then transplanted into 20-cm diameter pots and grown in a greenhouse at 25°C in natural day length, to growth stages 13 to 21.<sup>13</sup>

A factorial layout of four randomized blocks (Table 1) was used. Two postemergent grass-killing herbicides, diclofop-methyl and flamprop-methyl, with or without the adjuvants Howet and Ulvapon were tested. Howet was used at 0.25% (v/v) and Ulvapon at 2.0% (v/v). The spray solutions were applied with a laboratory track sprayer using two Spraying



TABLE 1  
Spray Treatments Tested

Adjuvant	Diclofop-methyl (1 ha <sup>-1</sup> )							Flamprop-methyl (1 ha <sup>-1</sup> )					
	0	0.05	0.1	0.2	0.4	0.8	1.6	0	1.0	2.0	4.0	8.0	16
None	X	X	X	X	X	X	X	X	X	X	X	X	X
Howet (0.25%)	X	X	X	X	X	X	X	X	X	X	X	X	X
Ulvapron (2.0%)	X	X	X	X	X	X	X	X	X	X	X	X	X

Systems flat fan 110015 nozzles at 190 kPa, each delivering 500 ml min<sup>-1</sup>, thus giving an application of 50 l ha<sup>-1</sup> at 12 km hr<sup>-1</sup>. The distance between the nozzle and the top of the plant canopy varied from 28 to 36 cm. After each spray, five plants per pot were harvested to assess spray collection; the remaining five plants were grown for 20 to 22 d to examine the biological effect.

### B. DROPLET SPECTRA OF THE SPRAY SOLUTIONS

Droplet spectra were measured using a laser diffraction technique (Malvern 2200 particle size analyzer) by passing the laser through the long axis of the spray fan produced by a Spraying Systems flat fan 110015 nozzle operated at 190 kPa, 10 cm from the orifice.<sup>1</sup> The data collected were fitted to a Rosin-Rambler distribution model and the volume of the spray in the diameter ranges 0 to 100, 100 to 300, >300 µm calculated.

### C. MEASUREMENTS OF SPRAY RETENTION

Each spray solution contained 0.4 g l<sup>-1</sup> Na-fluorescein to enable spray retention to be determined.<sup>11</sup> The five plants per pot harvested were cut into three parts: meristematic region (base) and lower (middle) and upper (top) half of leaves (Figure 1). The plant parts were washed in 30 ml of a 0.005 M NaOH solution for 30 s immediately following harvest to remove the Na-fluorescein. The washing solution was analyzed in a spectrophotometer at 495 nm. Leaf area was measured using a Paton planimeter. This enabled retention of spray solution to be expressed as quantity unit leaf area.

### D. STATISTICAL ANALYSIS

Analysis of the fresh and dry weight data was carried out using a parallel line assay technique as described by Streibig and Thonke,<sup>12</sup> thus, the data were fitted to a sigmoid model of the form:

$$E(U) = D - C/[1 + \exp \{-2(a + b \cdot \log(z))\}] + c, b < 0$$

The upper limit D denotes the expected plant response, E(U), at zero dose, while the lower limit C denotes the value of E(U) at large doses. The linear term  $\{a + b \cdot \log(z)\}$  shows that the responses on a logit scale can be represented as straight lines.<sup>12</sup>

## III. RESULTS

### A. SPRAY RETENTION BY PLANT PART

Spray retention by the top and middle of the leaf and basal parts of the plant are illustrated in Figures 2 and 3. With diclofop-methyl, retention of spray was similar for the top and middle of the leaf and significantly ( $p < 0.05$ ) lower than that of the basal part. With flamprop-methyl, however, retention by the top of the leaf was significantly ( $p < 0.05$ ) higher than that of the middle, which in turn retained significantly ( $p < 0.05$ ) more than the basal part of the plant.

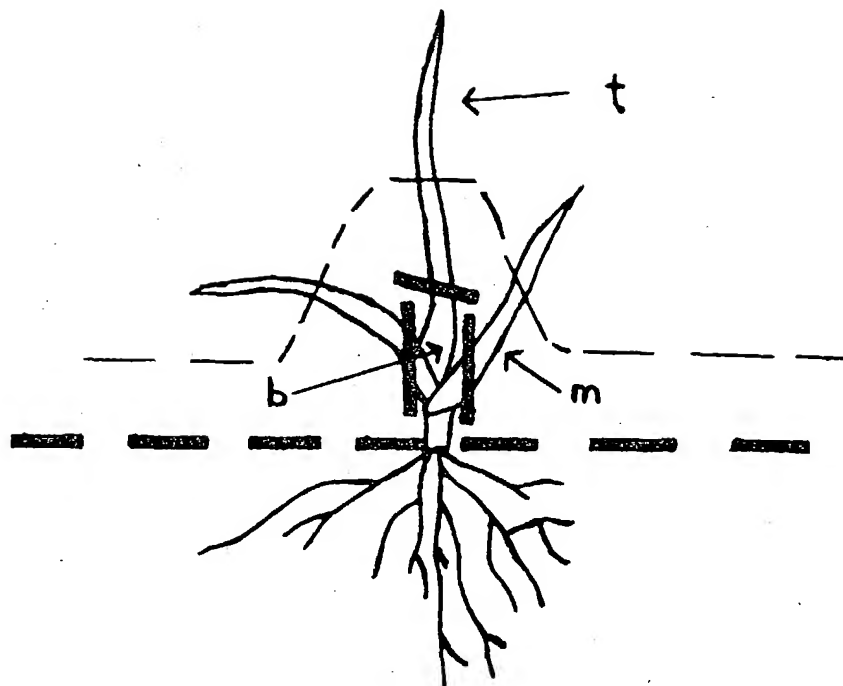


FIGURE 1. Illustration of the top (t) and middle (m) of leaf and basal (b) area of the plant.

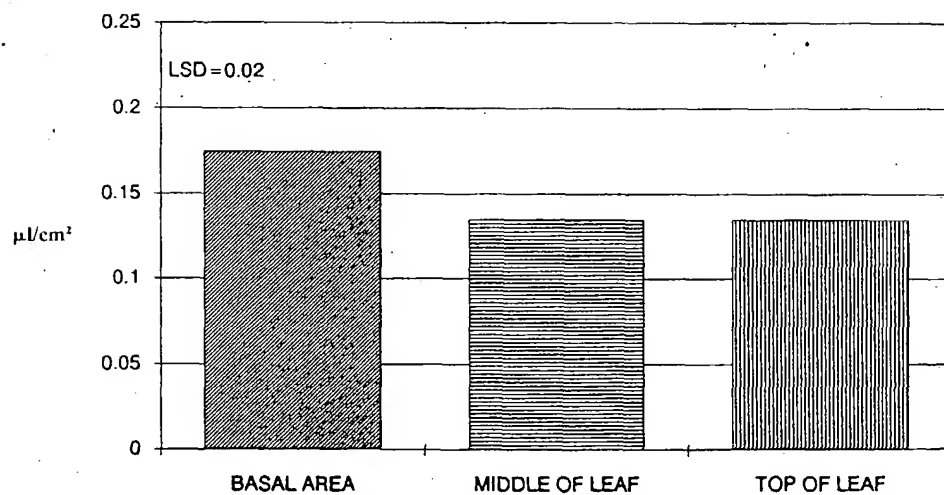


FIGURE 2. Retention of diclofop-methyl by plant part.

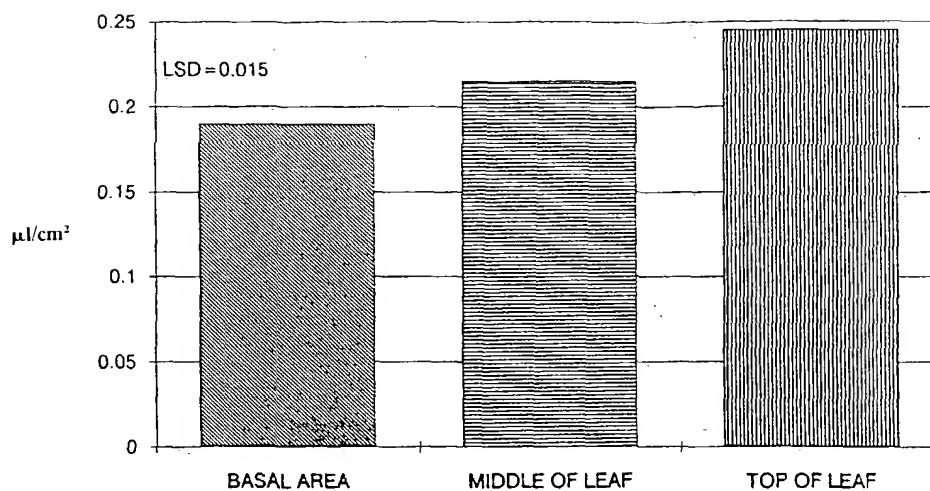


FIGURE 3. Retention of flamprop-methyl by plant part.

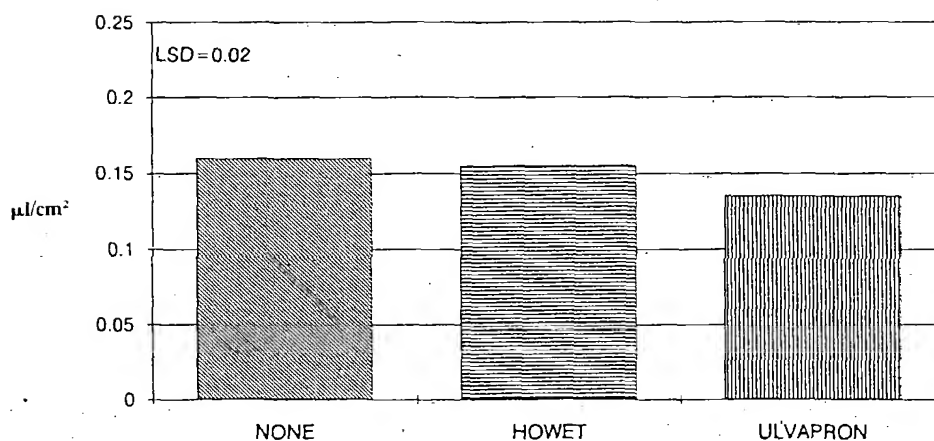


FIGURE 4. Effect of adjuvant on retention of diclofop-methyl.

Using a t-test, it was found that significantly ( $t_{172,0.05} = 12.88$ ) more flamprop-methyl was retained than diclofop-methyl on both the top and middle of the leaf. Retention by the basal part of the plant did not differ significantly between the herbicides.

#### B. INFLUENCE OF ADJUVANT ON SPRAY RETENTION

Retention was not altered with the addition of Howet or Ulvapon to diclofop-methyl (Figure 4). However, addition of Ulvapon to flamprop-methyl (Figure 5) resulted in a significantly ( $p < 0.05$ ) higher retention than the herbicide alone or with Howet.

A t-test to compare spray retention between the herbicides showed that plants treated with flamprop-methyl retained significantly ( $t_{172,0.05} = 12.94$ ) more spray than plants treated with diclofop-methyl when combined with either of the adjuvants or when used alone.

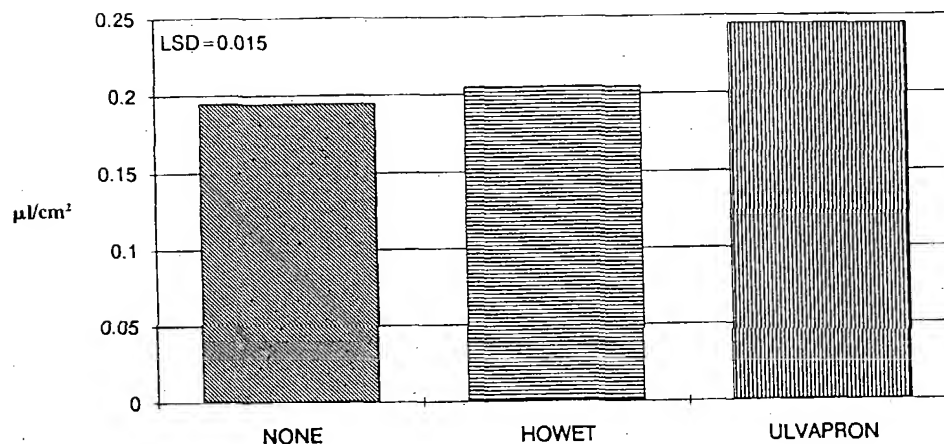


FIGURE 5. Effect of adjuvant on retention of flamprop-methyl.

TABLE 2  
Droplet Spectra Produced by the Spray Solutions Using  
a 110015 Flat Fan at 190 kPa

Adjuvant	Diclofop-methyl (l ha <sup>-1</sup> )							Flamprop-methyl (l ha <sup>-1</sup> )						
	0	0.05	0.1	0.2	0.4	0.8	1.6	0	1.0	2.0	4.0	8.0	16	
Percentage Weight <100 µm														
None	11.8	7.0	6.8	6.0	6.0	6.3	7.0	10.3	7.7	8.5	9.9	11.7	14.0	
Howet (0.25%)	15.3	7.5	7.5	7.0	6.3	8.0	11.1	15.3	8.0	8.0	10.7			
Ulvapron (2.0%)	6.8	6.8	7.2	7.4	6.1	6.4	6.4	6.8	7.3	7.5	10.4			
Percentage Weight between 100 and 300 µm														
None	66.9	73.9	73.7	73.5	72.1	73.2	73.5	66.8	76.0	77.7	78.4	78.8	77.2	
Howet (0.25%)	69.0	72.2	72.8	70.8	76.6	72.7	62.3	69.0	77.9	78.2	78.7			
Ulvapron (2.0%)	73.1	77.0	71.2	75.0	75.1	77.0	77.6	73.1	75.5	79.5	79.4			
Percentage Weight >300 µm														
None	21.2	19.5	19.0	20.7	21.6	20.4	19.5	22.9	16.2	13.8	11.6	9.5	8.8	
Howet (0.25%)	15.8	20.3	19.7	22.2	18.1	19.3	26.7	15.8	14.0	13.7	10.6			
Ulvapron (2.0%)	20.1	16.2	18.6	17.4	18.7	16.6	16.1	20.1	17.2	13.0	10.5			

### C. DROPLET SPECTRA

Increasing the concentration of diclofop-methyl did not change the droplet spectra when assessed with 0.25% (v/v) Howet or 2.0% (v/v) Ulvapron (Table 2). With flamprop-methyl, higher concentrations increased the small-droplet (<100 μm) component, while the large-droplet (>300 μm) component decreased (Table 2). Both Howet and Ulvapron accentuated this effect.

Both herbicides, when added to water or Howet + water, reduced the percentage of small droplets, but did not when added to Ulvapron + water.



TABLE 3  
Summary of Regression Analyses and Potency Estimates for Diclofop-Methyl, with  
and without Adjuvants

Spray	D (g/pot)	C (g/pot)	Logit = $-(a + b \log(z))$	ED <sub>50</sub> (l ha <sup>-1</sup> )	Relative potency
Fresh Weight					
Diclofop-methyl + water	21.58 (1.38)	3.99 (1.25)	$-0.044 + 5.570 \log(z)$ (0.687) (1.751)	1.018*	—
Diclofop-methyl + 0.25% Howet	—	—	—	0.743	1.371 (0.562)
Diclofop-methyl + 2.0% Ulvapon	—	—	—	0.404	2.522 (0.764)
Dry Weight					
Diclofop-methyl + water	4.184 (0.641)	1.316 (0.587)	$-1.687 + 17.47 \log(z)$ (9.613) (21.28)	1.249*	—
Diclofop-methyl + 0.25% Howet	—	—	—	0.801	1.560 (3.163)
Diclofop-methyl + 2.0% Ulvapon	—	—	—	0.403	3.103 (4.499)

Note: Standard deviations in parentheses; D, upper limit; C, lower limit.

\* ED<sub>50</sub> = antilog  $(-a/b)$ .

#### D. BIOLOGICAL EFFECT

The data showed a significant ( $p < 0.05$ ) interaction between the effect of herbicide and adjuvant for both herbicides. The results showed enhanced efficacy of the herbicides when mixed with adjuvant, on both a fresh and dry weight basis (Tables 3 and 4). Ulvapon consistently improved the efficacy of both herbicides more than Howet.

Diclofop-methyl + 0.25% (v/v) Howet or 2.0% (v/v) Ulvapon produced an equivalent biological effect (based on 50% effect level, Table 3) at 37 and 69% of the rate when used alone, respectively. An equivalent biological effect for flamprop-methyl alone was achieved at 74% of the rate when 2.0% (v/v) Ulvapon or 0.25% (v/v) Howet was added.

#### IV. DISCUSSION

The reductions in the small-droplet ( $< 100 \mu\text{m}$ ) spectra observed are possibly an effect of oil, as when the emulsifiable oil Ulvapon is added to water, the volume of small droplets is reduced. This has been previously reported by Dempsey et al.<sup>2</sup> and Moerkkerk et al.<sup>9</sup> However, when Howet is added, it increases the small-droplet component, which confirms the findings of McShane.<sup>7</sup> It was found that the herbicides which use oil as a solvent reduced the small-droplet component. Calculations show that the oil concentration at which the small-droplet spectra are reduced is  $> 0.01\%$  (v/v). The consequence of increasing the small-droplet component is to make the spray more prone to drift.<sup>2</sup> It is concluded that differences in spray retention do not arise from the small differences in droplet spectra.

Moser et al.<sup>10</sup> showed that the biological effect of four postemergent grass herbicides was greatest when placed on the basal part of the plant and least when placed on leaf tips. Similar results were found by Koch and Muller,<sup>5</sup> using diclofop-methyl on wild oats.



TABLE 4  
Summary of Regression Analyses and Potency Estimates for Flamprop-Methyl, with and without Adjuvants

Spray	D (g/pot)	C (g/pot)	Logit = $-(a + b \log(z))$	ED <sub>50</sub> (l ha <sup>-1</sup> ) <sup>a</sup>	Relative potency
Fresh Weight					
Flamprop-methyl + water	20.09 (1.57)	5.41 (0.96)	$-0.562 + 20.99 \log(z)$ (5.495) (263)	0.940 <sup>a</sup>	—
Flamprop-methyl + 0.25% Howet	—	—	—	0.871 (16.512)	1.079
Flamprop-methyl + 2.0% Ulvapron	—	—	—	0.996 (13.491)	0.944
Dry Weight					
Flamprop-methyl + water	9.88 (18.52)	1.22 (0.70)	$1.774 + 1.878 \log(z)$ (4.483) (3.558)	0.114 <sup>a</sup>	—
Flamprop-methyl + 0.25% Howet	—	—	—	0.020	5.69 (8.05)
Flamprop-methyl + 2.0% Ulvapron	—	—	—	0.001 (6.5)	172

Note: Standard deviations in parentheses; D, upper limit; C, lower limit.

<sup>a</sup> ED<sub>50</sub> = antilog  $(-a/b)$ .

For flamprop-methyl, retention was greatest on the top of the leaves (Figure 3). With diclofop-methyl, the first five dose rates did not produce a significant ( $p > 0.05$ ) biological effect and retention was greatest for the basal plant part (Figure 2). Thus; while the distribution of spray with diclofop-methyl is better than with flamprop-methyl according to Moser et al.<sup>10</sup> and Köch and Muller,<sup>5</sup> this was not reflected as efficacy in these tests. Two possible explanations are (1) the other groups brushed or painted the herbicides onto the plant, which may have altered the physical state of the plant surface, whereas these treatments were applied as spray, or (2) it may well be that the differing results have arisen from environmental differences. McLaughlan<sup>6</sup> and Devine<sup>4</sup> discuss the many environmental influences on herbicide performance.

The results in Table 3 for diclofop-methyl show that the addition of both Howet and Ulvapron increase the relative potency of this herbicide. However, with flamprop-methyl, there is a similar improvement with respect to dry weight but not fresh weight. In view of the variability in the tests carried out using flamprop-methyl, conclusions derived from these data must be viewed with caution.

Only the 2.0% (v/v) Ulvapron + flamprop-methyl spray solution improved spray retention on the plants. This may be an effect of oil as, in general, adjuvants did not significantly ( $p > 0.05$ ) improve herbicide retention. This agrees with the findings of Dempsey et al.<sup>2</sup> for 2,4-D amine and ester on ryegrass (*Lolium rigidum*, Gaud.) and de Ruiter and Uffing<sup>3</sup> on couch grass (*Elymus repens* (L.) Gould). The latter authors, using scanning electron microscopy, showed that surfactants did not improve retention on plant species with smooth cuticular surfaces, and that the nature of the cuticular surface appeared to be the main factor determining retention. It is possible that Howet did not improve retention on wild oat for reasons similar to that advanced by de Ruiter and Uffing.<sup>3</sup> Therefore, enhanced herbicidal efficacy is not simply a result of improved retention. Similarly, Moerkert et al.<sup>9</sup> concluded that adjuvants did not improve spray retention, yet enhanced the efficacy of diclofop-methyl on wild oats.

While the mechanism for improving efficacy by adjuvants remains unclear, the results show that the dose of the herbicides tested can be reduced if an appropriate adjuvant is used. By using Ulvapon at 2.0% (v/v), rates of diclofop-methyl and flamprop-methyl can be reduced by 20 and 55%, respectively, without loss of efficacy. With Howet, rate reductions of 10% (diclofop-methyl) and 55% (flamprop-methyl) are implicated. This will enable a reduction in environmental contamination while maintaining the same control.

Further, as the adjuvants used are cheaper than the herbicides, their use can reduce the cost of weed control. For example, 2.0% (v/v) Ulvapon added to one third the normal diclofop-methyl rate produces a biological effect similar to diclofop-methyl alone. The savings to the farmer is equivalent to the reduction in diclofop-methyl dosage times its cost minus the dosage of Ulvapon times its cost.

### ACKNOWLEDGMENT

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## Chapter 32

**EFFECT OF A SYNTHETIC POLYMER ON ADSORPTION AND  
LEACHING OF HERBICIDES IN SOIL**

Rakesh Jain and Megh Singh

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## I. INTRODUCTION

### A. LOSSES OF HERBICIDES IN SOIL

Herbicides are an essential part of modern techniques in horticultural and agricultural production systems. A majority of the herbicides used today are applied directly to the soil, a common medium for growth of weed and crop plants. Herbicides also reach the soil indirectly by such means as runoff from plant foliage. Ideally, a herbicide, when applied to the soil, should reach its target in the plant root zone in sufficient concentration to control weeds for a desired length of time and then dissipate quickly without harming the environment.<sup>17,18,41</sup> Few herbicides, however, fall into this category. Conventionally, most herbicides are applied at rates much higher than those that would actually be required for weed control under ideal conditions. These higher rates of herbicides are applied mainly to offset losses that occur from their site of action in the plant root zone.<sup>49,53</sup>

Losses of herbicides from the plant root zone occur by several physical, chemical, and biological processes.<sup>34</sup> When lying on the surface of the soil, herbicides can be lost by volatilization or photodecomposition. Once they move into the soil profile, they can be degraded chemically or biologically, adsorbed by soil colloids, taken up by plants, or leached to the lower layers of the soil profile.<sup>23,30</sup> The amount of herbicides lost by each of these processes varies greatly from region to region, depending upon soil type and environmental factors, including rainfall. In Florida, for example, considerable loss of herbicides applied to the soil occurs by leaching due to the extremely permeable nature of the soil (90% or more sand) and the high amount (135 cm) of rainfall received per year.<sup>37,71,77</sup>

Besides the nature of the soil and the amount of water that percolates through it, the extent of loss also depends upon the herbicide properties.<sup>80,81</sup> Mobility of five thiocarbamate herbicides was found to be directly correlated with water solubility.<sup>27,42</sup> Similar correlations between solubility and herbicide leaching have been reported by Baker et al.<sup>4</sup> Other properties that influence pesticide behavior in soil are chemical structure, vapor pressure, adsorption coefficient, and persistence. These factors have been reviewed by Bailey and White,<sup>3</sup> Hartley,<sup>34</sup> Helling,<sup>35</sup> and Weber.<sup>81</sup>

Groundwater contamination from agrichemicals is a growing concern in the U.S. and many other developed countries. Reports in the literature have indicated that more than 12 different pesticides have been detected in the groundwater of at least 24 states in the U.S. as a result of routine agricultural use.<sup>15,29</sup> The fraction of the dose of a pesticide leached into groundwater is generally less than 1%.<sup>7</sup> Few long-term data exist, but studies conducted in Iowa suggest that pesticide residues in groundwater are increasing, perhaps in a manner analogous to the rise in nitrate concentration of a decade ago.<sup>28</sup> Bromacil (chemical names of pesticides included in the text are listed in Table 1) has been found in the groundwater in Florida in concentrations as high as 300  $\mu\text{g/l}$ .<sup>58</sup> Aldicarb carbamate residues were detected in drinking water on Long Island, New York in 1979,<sup>29,83</sup> and more recently in Florida in concentrations ranging from 1 to 50  $\mu\text{g/l}$ .<sup>58</sup> The timing and quantity of aldicarb application have been restricted on a crop-by-crop and geographic basis in Florida. Under a Health and Rehabilitative Services surveillance program, of the 6712 drinking water wells in 64 counties in Florida monitored for ethylene dibromide (EDB) residues, 733 wells were found to contain the chemical in amounts ranging up to 710 ppb. The state-wide range for positive wells was 6.5 ppb of EDB, well above the federal and state action level of 0.02 ppb.<sup>67</sup> The Environmental Protection Agency has suspended all uses of EDB for soil fumigation in the U.S. since September 30, 1983, due to its environmental and health hazards. The most frequently detected pesticides in groundwater in western Europe have been triazines, such as atrazine and simazine, and some of their transformation products in concentrations ranging from 0.01 to 1  $\mu\text{g/l}$ .<sup>45</sup> Besides these chemicals, alachlor, bentazon, carbofuran, cyanazine, di-



TABLE 1  
Common and Chemical Names of Pesticides Included in the Text

Common name	Chemical name
Alachlor	2-Chloro- <i>N</i> -(2,6-diethylphenyl)- <i>N</i> -(methoxymethyl) acetamide
Aldicarb	2-Methyl-2-(methylthio)propionaldehyde- <i>O</i> -(methyl-cabamoyl)oxime
Anisomycin	2-(4-Methoxyphenylmethyl)-3,4-pyrrolidinediol-3-acetate
Atrazine	6-Chloro- <i>N</i> -ethyl- <i>N'</i> -(1-methylethyl)-1,3,5-triazine-2,4-diamine
Bentazon	3-(1-Methylethyl)-(1 <i>H</i> )-2,1,3-benzothiadiazin-4(3 <i>H</i> )-one 2,2-dioxide
Bialaphos	L-2-Amino-4-[(hydroxy)(methyl)phosphinoyl]-butyryl-L-alanyl-L-Alanine
Bromacil	5-Bromo-6-methyl-3-(1-methylpropyl)-2,4-(1 <i>H</i> ,3 <i>H</i> ) pyrimidinedione
Butylate	<i>S</i> -Ethyl-bis(2-methylpropyl)Carbamathioate
Carbofuran	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate
Chloramben	3-Amino-2,5-dichlorobenzoic acid
Chlortoluron	3-(3-Chloro-4-methylphenyl)-1,1-dimethylurea
Cyanazine	2-[[4-Chloro-6-(ethylamino)-1,3,5-triazine-2-yl]amino]-2-methylpropanenitrile
2,4-D	(2,4-Dichlorophenoxy) acetic acid
Dicamba	3,6-Dichloro-2-methoxybenzoic acid
Dinoseb	2-(1-Methylpropyl)-4,6-dinitrophenol
Diquat	6,7-Dihydrodipyrido[1,2- $\alpha$ :2',1'- <i>c</i> ] pyrazinedium ion
Diuron	<i>N'</i> -(3,4-dichlorophenyl)- <i>N,N</i> -dimethylurea
EDB	Ethylenedibromide
EPTC	<i>S</i> -ethyl dipropylcarbamathioate
Glyphosate	<i>N</i> -(phosphonomethyl)glycine
Linuron	<i>N'</i> -(3,4-dichlorophenyl)- <i>N</i> -methoxy- <i>N</i> -methylurea
Mecoprop	( $\pm$ )-2-(4-Chloro-2-methylphenoxy)propanoic acid
Metribuzin	4-Amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4 <i>H</i> )-one
Monuron	<i>N'</i> -(4-chlorophenyl)- <i>N,N</i> -dimethylurea
Norflurazon	4-Chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(2 <i>H</i> )-pyridazinone
Prometryn	<i>N,N'</i> -bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
Rhizobitoxin	2-Amino-4-(2-amino-3-hydroxypropoxy)-3-butenic acid
Simazine	6-Chloro- <i>N,N</i> -diethyl-1,3,5-triazine-2,4-diamine
Tentoxin	Cyclic ( <i>N</i> -methyl-L-alanyl-L-leucyl- $\alpha,\beta$ -didehydro- <i>N</i> -methylphenylalanyl)glycyl
Terbacil	5-Chloro-3-(1,1-dimethylethyl)-6-methyl-2,4(1 <i>H</i> ,3 <i>H</i> ) pyrimidinedione
Trifluralin	2,6-Dinitro- <i>N,N</i> -dipropyl-4-(trifluoromethyl) benzeneamine

noseb, mecoprop, metribuzin, and terbacil also have been found in significant amounts in several countries.<sup>15,29,37,45</sup>

## B. METHODS OF REDUCING HERBICIDE LEACHING IN SOIL

Several methods have been tried to prevent leaching of herbicides in soil. One of these approaches is the use of alternative herbicides, which are less mobile in soil. Chemicals most likely to succeed as alternative herbicides are those that have a high adsorption capacity, low water solubility, and a short persistence in soil. Alternative herbicides are not always available, however, for weed control in certain crops. Several naturally occurring products including allelochemicals, can also have the potential to become alternative herbicides.<sup>56,66</sup> Some examples of naturally occurring phytotoxins are anisomycin, bialafos, rhizobitoxin,<sup>9</sup> and tentoxin.<sup>21</sup> Much research remains to be done, however, before allelochemicals are commercially used for weed control.

Another approach for reducing herbicide leaching in soil and subsequently into the groundwater is aimed at reducing the effective concentration of chemicals in the soil. Some of the new herbicides, such as sulfonylureas, are used at very low rates, and thus have lower potential of reaching the groundwater.<sup>66</sup> Improved application technology can also reduce the amount of herbicide available for leaching to groundwater. Use of computer-controlled applicators, controlled droplet applicators, air curtain sprayers, spinning-disc sprayers, elec-



trostatic sprayers, and rope-wick applicators help to prevent over application and chemical waste and to increase the efficiency of herbicide application.<sup>54</sup>

In irrigated areas, the use of improved irrigation technology can also reduce herbicide leaching in soil. Trickle irrigation is a method used on orchards, vegetables, and ornamentals to supply water and minerals directly to the root system of growing plants. It consists of plastic tubes and nozzles through which water is discharged as a trickle at low pressure. The tubes and nozzles are located along crop rows such that the area across which infiltration takes place is very small compared with the total soil surface, and large areas between tubes and between nozzles remain dry.<sup>9,10,26</sup> The movement of water from trickle irrigation follows a three-dimensional pattern<sup>9</sup> in which the movement of a herbicide under trickle irrigation is parallel, to some extent, to that of the trickled water, but total herbicide movement is less than that of the water.<sup>43</sup> Both water and herbicide distribution in the soil form the shape of a hemisphere or cone under the trickle nozzle, the exact shape of which is determined by the soil characteristics (a narrow cone in a light soil and a wide cone in a heavy soil), and cone size is determined by the amount of trickle water. Thus, the total amount of herbicide applied to the soil can be reduced by applying the herbicide in a ring around the crop plants only and leaving the interplant areas untreated. It has been observed that the interplant areas have a negligible infestation of weeds due to the unavailability of water in the dry regions, and most soil-applied herbicides lose much of their potency in the dry areas, as there is no water to activate them.<sup>43</sup>

The use of activated charcoal is another way of preventing herbicide leaching in soil in the event of an application overdose or a chemical spill. The use of activated charcoal for detoxification purposes has been widely investigated.<sup>6,11,38,44,70,78</sup> By carefully adjusting the rate of activated charcoal applied to contaminated soil, a partial detoxification can be achieved by reducing the concentration sufficiently to not injure the crop but, at the same time, control weeds effectively. The effectiveness of activated charcoal to eliminate norflurazon injury to cotton without reducing prickly sida and seedling johnsongrass control has been demonstrated.<sup>44</sup> Activated carbon acts as a strong adsorbent due to its large surface area. Large amounts are often necessary for effective removal of the herbicide from soil solution, however, and not all forms of activated carbon adsorb equally.<sup>40</sup> Amounts required to remove organic herbicides from soil range from 50 to 400 kg of activated carbon per hectare for each kilogram of active ingredient (a.i.) per hectare of herbicide. Ratios of charcoal to herbicide as high as 3600:1 have been reported.<sup>8</sup>

### C. USE OF ADJUVANTS FOR REDUCING HERBICIDE LEACHING IN SOIL

Adjuvants have been used extensively to alter the activity of herbicides on plants. Little information is available, however, concerning their effects on the behavior of pesticides in the soil. A recent approach by which certain adjuvants bind the herbicide molecules and then release them slowly over time holds considerable promise in preventing excess herbicide leaching in soil. This approach of binding the herbicide and then slowly releasing it in soil is termed slow release or controlled release.<sup>16,17</sup> The release of a.i. in a controlled manner may not only reduce groundwater contamination, but may also enhance the efficacy of the herbicides by reducing their losses in the soil. An excellent review on the controlled release of herbicides has recently been written by Schreiber et al.<sup>64</sup>

Adjuvants can be either formulated with the herbicides or added to spray solutions just before spraying. In either case, the objective of adding a surfactant is to bind the herbicide molecule so that it is not subjected to leaching or other losses in the soil. A herbicide can be chemically attached to, or physically entrapped within, another substance such as a polymer. The resulting complex contains the herbicide in a manner capable of being released upon hydration, hydrolysis, erosion, biodegradation, diffusion, osmosis, mechanical rupture, or other suitable means.<sup>64</sup>

Bayer<sup>5</sup> first indicated that downward movement of substituted urea herbicides, diuron, linuron, and monuron could be eliminated completely with the use of certain cationic surfactants. Diuron, which shows affinity for certain lipophilic materials, adsorbed onto soil particles by Van der Waal's forces, thereby removing itself from solution, but not from absorption by plant roots. Early experiments with several surfactants proved unsuccessful in preventing the leaching of metribuzin in soil.<sup>55,62,79</sup> In later experiments, however, the mobility of metribuzin in soil was successfully reduced when the herbicide was formulated with polymers of polyvinyl alcohols.<sup>31,52</sup> One disadvantage of using this type of formulation was that metribuzin formed covalent linkages with the polyvinyl alcohols, which resulted in the dependence of the release of metribuzin from the polymer for uptake by plants upon soil-related enzymatic reactions.

Certain pine kraft lignins have been tested for the controlled release of several herbicides. Dunigan and McIntosh<sup>22</sup> observed that pine kraft lignin bound to atrazine and DelliColli<sup>19</sup> reported that kraft lignins could be successfully used to prevent the loss of 2,4-D from soil. Pine kraft lignins, NB-5203-58 and PC940 series, adsorbed and desorbed metribuzin on soil thin-layer chromatography plates. PC940C also provided controlled release of alachlor,<sup>61</sup> metribuzin, and chloramben<sup>60</sup> as measured by water leaching in soil columns. PC940C itself was immobile in soil columns leached with water.<sup>61</sup> Pine kraft lignin is a product of the alkaline wood pulping process.<sup>50</sup> It has a large number of hydroxyl, carboxylic, and keto groups,<sup>19</sup> which may participate in hydrogen bonding of pesticides. In addition, kraft lignin has been found to consist of cross-linked polymers,<sup>50</sup> which may have the potential to entrap both metribuzin and alachlor. Madhun et al.<sup>47</sup> reported that herbicides such as bromacil, diuron, chlortoluron, simazine, glyphosate, and diquat bound to water-soluble soil organic materials (WSSOM), which consist of compounds with molecular masses in the range of 700 to 5000 Da and resemble very closely the fulvic acids present in soil and surface waters. Madhun et al.<sup>46</sup> have also reported on the binding of pesticides by humic substances, such as humic and fulvic acids.

Besides pine kraft lignins, three other adjuvants, ARD 54, ARD 93, and ARD 1836, have proved effective in reducing metribuzin injury on soybeans and increasing sicklepod control.<sup>73</sup> These adjuvants were tertiary amines with one fatty alkyl group, derived from fatty sources with 12 to 18 carbon atoms and two polyoxyethylene groups attached to the nitrogen. All were produced from primary fatty amines. These adjuvants slightly reduced the movement of metribuzin in thin-layer chromatography, but had no effect on sorption in batch-equilibrium experiments.<sup>73</sup>

Formulations of pesticides as granules, where the pesticide is entrapped within a starch matrix, have made considerable progress over the last decade.<sup>60,69,75,76</sup> Initially, much of the interest in starch (xanthide and borate) formulations involved thiocarbamate and dinitroaniline herbicides that are relatively insoluble in water and are subject to losses resulting from volatilization.<sup>14,20,25,63,65,68</sup> Later, several starch xanthide formulations of chloramben were tested successfully for increasing weed control efficiency of the herbicide in pumpkin (*Cucurbita moschata*) resulting mainly from reduced leaching losses.<sup>57</sup> Leaching of chloramben occurs when it is formulated as the ammonium salt of benzoic acid, which is very soluble in water (700 ppm at 25°C), dissociates, and carries a negative charge at typical crop-production soil pHs.<sup>24</sup> Therefore, the ammonium salt is not adsorbed in most soils and is subject to loss by leaching. Some polysaccharides have also proved effective in reducing metribuzin mobility in soils.<sup>51</sup> One drawback of using polysaccharide formulations is that polysaccharides can serve as a readily available carbon source for soil microorganisms, which can shorten the life of the controlled-release agent.

In contrast to the polysaccharides, highly persistent polymer solid matrices, such as polyvinyl chloride<sup>72</sup> and polyethylene,<sup>33</sup> have been used to incorporate phenoxy herbicides

TABLE 2  
Physical and Chemical Characteristics of Herbicides Used in This Investigation

Herbicide	Solubility in water at 25°C (ppm)	Partition coefficient $K_{oc}$ (mg/l)	Ionizability (pKa)	Half-life ( $T_{1/2}$ ) (d)	Leaching potential ( $K_{oc}/T_{1/2}$ )
Bromacil	815	72	Acidic (9.1)	90	0.8
Simazine	5	138	Basic (1.65)	75	1.9
Norflurazon	28	248	Nonionic	45	5.5
Diuron	42	400	Nonionic	100	4.0

to provide long-term control of *Myriophyllum spicatum* in an aquatic system. Other controlled-release formulations of the butoxyethanol ester of 2,4-D that have been tested successfully against *M. spicatum* include rubber-based compounds formulated as sinking pellets that slowly release the herbicide.<sup>12</sup> Certain hydrophilic polymers that contain a high percentage of phenoxy herbicides as pendant side chains,<sup>32</sup> such as in the case of 2,4-D/poly(glycidyl methacrylate), have also been used as controlled-release agents. In such formulations, herbicide release occurs by the slow, sequential hydrolysis of the herbicide-polymer chemical bonds. Such herbicide-polymer formulations have, however, not been tested for controlled release of pesticides in soil systems. The purpose of the following investigation was to determine the effect of a synthetic polymer on herbicide efficacy and leaching in soil.

## II. MATERIALS AND METHODS

### A. EXPERIMENTAL PROCEDURES

#### 1. Soil Properties

The soil used in the following investigations was Astatula fine sand (Quartzipsamment sandy entisol) with a low cation exchange capacity ranging from 1 to 4 meq/100 g.<sup>1</sup> Percent sand, silt, and clay contents were 96.5, 2.0, and 1.5, respectively. Organic matter content was about 1% and the pH of the soil was 6.5. The soil had a low water-holding capacity ranging from 0.5 to 1.2 cm of water per 15 cm of soil.

#### 2. Source of the Polymer

The polymer, STAY-TEC,<sup>®</sup> was obtained from Delacar Corp. of Tavares., FL. It was a commercial formulation consisting of 25% hydrophilic polymer and 75% inert material. Information on the physical and chemical properties of the polymer is not available at present.

#### 3. Effect of STAY-TEC on Herbicide Efficacy

The effect of STAY-TEC on the efficacy of four herbicides (bromacil, diuron, norflurazon, and simazine) was investigated in field and greenhouse experiments. The physical and chemical properties of the herbicides are presented in Table 2. The experiment in the field was conducted in a young citrus (Nova on Milam) grove located near the Citrus Research and Education Center in Lake Alfred, FL. The soil type was as described above. The dominant weeds in the field were Florida pusley (*Richardia scabra*), guineagrass (*Panicum maximum*), wild watermelon (*Citrullus vulgaris*), and common ragweed (*Ambrosia artemisiifolia*).

The experiment was started in June 1989 by disking the field twice to kill the existing weed plants. Herbicides were applied 1 d after disking the plots. Bromacil (Hyvar L) and norflurazon (Solicam DF) were applied at 1.6 or 3.2 kg a.i./ha and diuron (Direx 4L) and simazine (Princep 4L) were applied at 2.0 or 4.0 kg a.i./ha, alone and in combination with STAY-TEC. In treatments containing STAY-TEC, the polymer was added to the spray tank

at the rate of 8.3 l/ha. Treatments were applied with a tractor-mounted sprayer calibrated to deliver 250 l/ha. Untreated plots were also included. All treatments were replicated three times in a randomized complete block design.

Weed control was evaluated visually 4 weeks after treatments and at regular intervals thereafter. Results presented are for percent weed control 60 and 120 d after treatment.

The greenhouse experiment was conducted in 20 × 20 × 5-cm aluminum trays filled with soil. The soil type was the same as that in the field experiment. Yellow foxtail (*Setaria glauca*), Florida pusley, and stranglevine (*Morrenia odorata*) seeds were planted in rows in each tray. Herbicide treatments were applied preemergence with commercial formulations of bromacil, diuron, norflurazon, and simazine at 62.5, 125.0, 250.0, or 500.0 g a.i./ha, alone or in combination with STAY-TEC. In treatments containing STAY-TEC, the polymer was mixed with the spray solution at the rate of 0.5% (v/v). Treatments were applied with a tractor-mounted sprayer calibrated to deliver 250 l/ha. The trays were watered daily with a sprinkler. Observations on weed control were recorded visually at 2-week intervals after treatment. Shoot numbers and fresh weights were obtained 6 weeks after treatment.

After all the existing shoots were removed, the trays were planted again with the same three weeds in rows running across the previous rows. Observations on weed control were recorded again visually at 2-week intervals, and shoot numbers and fresh weights of weeds were obtained 6 weeks after replanting.

#### 4. Effect of STAY-TEC on Herbicide Adsorption and Desorption

The effect of STAY-TEC was investigated on adsorption and desorption of the four herbicides, bromacil, diuron, norflurazon, and simazine, on soil. These herbicides represented a wide range of physical and chemical properties (Table 2). Also, all four herbicides are commonly used for weed control in Florida citrus groves.

Two different methods were used to investigate the adsorption and desorption of herbicides on soil. The first method was a slight modification of the batch-equilibrium method described by Rhodes et al.<sup>59</sup> In this method, 2.5 g of screened and oven-dried soil were mixed with 3 ml of the herbicide solution to obtain a slurry. Herbicide solutions were prepared in ethanol by dissolving a mixture of the <sup>14</sup>C-labeled and technical grade, nonradioactive herbicide. A small volume of these herbicide solutions was pipetted into 7.4-ml glass sample vials. The ethanol was allowed to evaporate and then 3 ml of deionized water were added to each vial. In treatments containing the polymer, STAY-TEC was added at a concentration of 0.5% (v/v) to the herbicide solution. The final herbicide concentration in the vials ranged from 1 to 20 ppm, and each vial contained about 5000 dpm (disintegrations per minute) of radioactivity. The soil was added to herbicide solutions. Since adsorption in this method was presumed to occur on wet soil, this method was termed the wet soil method.

In the second method, developed by Majka and Lavy,<sup>48</sup> 2.5 g of oven-dried soil were first poured into clean 7.4-ml glass sample vials and 100 µl of the herbicide solution were added directly to the soil and mixed thoroughly. The soil was then allowed to dry in a hood overnight. In treatments containing the polymer, STAY-TEC was added to the herbicide solutions before they were added to the soil. After the soil had dried, 3 ml of deionized water were added to each vial. The adsorption of herbicides in this method occurred on dry soil; therefore, this method was designated the dry soil method.

The soil slurries in both methods were shaken on a rotary-type mechanical shaker. The rate of shaking was adjusted to maintain the soil in complete suspension. To determine the length of time required for the soil slurries to reach equilibrium with the herbicides applied alone or in combination with STAY-TEC, the vials containing the slurries were shaken for 1, 4, 24, 48, or 72 h. The effect of polymer concentration on herbicide adsorption was investigated by mixing STAY-TEC with the herbicide solutions in concentrations ranging from 0 to 5% (v/v).



After shaking, the slurries were allowed to stand for about 2 h and then centrifuged at 15,000 g for 20 min. One milliliter (ml) of the clear supernatant was then removed from each vial and mixed with 10 ml of a commercially available scintillation cocktail (ScintiVerse<sup>®</sup> II, Fisher Scientific Co., Fairlawn, NJ 07410) to determine the amount of radioactivity remaining in the solution. The amount of herbicide adsorbed was then calculated by subtracting the amount of radioactivity in the soil solution from the total radioactivity applied. The results are expressed as a partition coefficient ( $K_d$ ), which is the ratio at equilibrium of the concentration of  $^{14}\text{C}$ -herbicide in the soil ( $C_s$ ) and the aqueous phase ( $C_w$ )<sup>74</sup> or the actual amount of herbicide adsorbed per gram of soil.

Desorption experiments were conducted to determine the mechanism of adsorption of the herbicides applied alone or in combination with STAY-TEC. In these experiments, the herbicides were allowed to adsorb on soil colloids and were then desorbed by successive additions and removals of 2 ml of deionized water or 1 *N*  $\text{CaCl}_2$ . Each time after the equilibrium was allowed to establish between the soil and the soil solution, 2 ml of the supernatant were counted in a liquid scintillation counter to determine the amount of radioactivity desorbed. The same volume of clean deionized water or 1 *N*  $\text{CaCl}_2$  was then added back to the mixtures and shaken again. This procedure was repeated for a total of four or five desorptions. Calcium chloride was used to determine whether a cationic exchange mechanism was involved in adsorption. A greater amount of herbicide would be desorbed with  $\text{CaCl}_2$  than with deionized water if a cationic exchange mechanism were involved. If not, then other forces such as Van der Waals' forces or hydrogen bonds were involved.

### 5. Effect of STAY-TEC on Herbicide Mobility

The mobility of herbicides in soil was determined using soil thin-layer chromatography (TLC).<sup>36</sup> Soil TLC plates were prepared by coating 20 × 20-cm glass plates with a 1-mm-thick layer of a soil slurry. The soil coating was allowed to dry and the  $^{14}\text{C}$ -labeled herbicides (with a total radioactivity of 50,000 dpm) alone or in combination with STAY-TEC were spotted 2.5 cm from the bottom edge of the plates. The plates were then developed with deionized water up to a height of 18 cm from the point of herbicide application. When the plates had dried, the soil in the developed area was divided laterally into ten 1-cm bands and scraped. The soil from each band was then shaken with 3 ml of water to desorb the herbicide. A portion of the supernatant was counted in a liquid scintillation counter to determine the amount of radioactivity present.

Herbicide movement was also studied using soil leaching columns.<sup>82</sup> PVC pipes 48 cm long with a 10-cm diameter were split longitudinally into halves. A ridge of silicone was applied on the inside wall of each half at a spacing of 15 cm. This was done to prevent the free flow of water along the interface of the soil and the PVC pipe. The two halves were joined and taped together to form a column. A PVC cap with a small plastic tube inserted in the center was fitted at the lower end of each column.

The columns were then packed with soil and stood upright with the help of a wooden frame. Before starting the experiment, the soil in each column was saturated with water and allowed to drain overnight. Commercial formulations of herbicides were applied at the top of the columns at rates of 4 to 5 kg/ha. Treatments were applied with or without STAY-TEC by first mixing 5 ml of the herbicide solution with 100 g of soil and then spreading the treated soil evenly on top of the columns. Irrigations were applied at two different rates. Deionized water was used for irrigation, which was applied at the top of the columns with the help of a sprinkler bottle at the rate of 1.25 or 2.5 cm/d in the case of bromacil and simazine, and 2.5 or 5 cm/d in the case of norflurazon and diuron for a total of 6 d. At the end of the irrigation treatments, the columns were allowed to drain completely and then cut open along the soil into halves. Each half was then planted with ryegrass in rows 5 cm



TABLE 3  
Effect of STAY-TEC® on the Efficacy of Four Herbicides  
for Weed Control in Citrus

Treatment*	Rate (lb a.i./A)	Days after application	
		60	120
Control		0	0
Bromacil	1.6	97	40
Bromacil + ST	1.6	95	65
Bromacil	3.2	95	77
Bromacil + ST	3.2	95	87
Diuron	2.0	98	95
Diuron + ST	2.0	98	96
Diuron	4.0	100	93
Diuron + ST	4.0	99	98
Norflurazon	1.6	84	65
Norflurazon + ST	1.6	91	83
Norflurazon	3.2	95	85
Norflurazon + ST	3.2	96	85
Simazine	2.0	92	25
Simazine + ST	2.0	95	32
Simazine	4.0	94	42
Simazine + ST	4.0	97	73
Least Significant Difference (LSD) (0.05)		9.6	9.7

\* STAY-TEC (ST) was added to herbicide solutions at the rate of 8.3 l/ha.

apart. Visual observations and fresh weight of ryegrass shoots were recorded 3 weeks after planting.

### III. RESULTS AND DISCUSSION

#### A. EFFECT OF STAY-TEC ON HERBICIDE EFFICACY

Results of the field experiment showed that all herbicides, except norflurazon applied at the lower rate, provided over 90% control of weeds when observations were recorded 60 d after treatment (Table 3). Percent weed control with herbicide treatments containing STAY-TEC did not differ significantly from that obtained with treatments containing the herbicides alone. The level of weed control was considerably lower in all plots treated with bromacil, norflurazon, or simazine alone 120 d after treatment. In plots treated with the herbicides applied in combination with STAY-TEC, however, percent weed control was significantly higher than in plots treated with the herbicides applied alone. Diuron applied alone or in combination with STAY-TEC provided excellent weed control 120 d after treatment.

In the greenhouse, simazine reduced the growth of yellow foxtail, Florida pusley, and stranglevine (Table 4). Florida pusley was most sensitive and stranglevine was most tolerant to the herbicide, especially at the lower rates. The addition of STAY-TEC to simazine solutions resulted in a reduction of the effect of the herbicide on the growth of all three species. There was no significant effect of STAY-TEC on the efficacy of bromacil, diuron, or norflurazon (data not presented). Replanting of the weed seeds 6 weeks after treatment, however, indicated that there was significantly less growth of weed plants in trays treated with simazine in combination with STAY-TEC than in trays treated with simazine alone (Table 4). Again, there was no significant effect of STAY-TEC on the efficacy of bromacil, diuron, or norflurazon (data not presented).

TABLE 4  
Effect of STAY-TEC on the Efficacy of Simazine for Weed Control

Treatment <sup>a</sup>	Rate (g/ha)	Percent control					
		First seeding			Second seeding <sup>b</sup>		
		Yellow foxtail	Stranglevine	Florida pusley	Yellow foxtail	Stranglevine	Florida pusley
Control		0	0	0	0	0	0
Simazine	62.5	17	30	70	13	20	97
Simazine + ST	62.5	2	10	67	60	53	98
Simazine	125.0	63	30	87	17	75	97
Simazine + ST	125.0	17	13	73	60	80	100
Simazine	250.0	87	57	100	73	93	100
Simazine + ST	250.0	63	53	93	80	100	100
Simazine	500.0	93	97	100	87	95	100
Simazine + ST	500.0	93	70	100	93	100	100
LSD (0.05)		13	22	12	11	19	9

<sup>a</sup> STAY-TEC (ST) was added to herbicide solutions at the rate of 0.5% (v/v).

<sup>b</sup> Second seeding was done 6 weeks after the first seeding. Observations on weed control were recorded 6 weeks after each seeding.

Controlled-release formulations have been reported to improve the overall effectiveness of agricultural chemicals and reduce toxicity to nontarget organisms. In laboratory experiments, Shreiber et al.<sup>63</sup> found that certain starch xanthide formulations of butylate and EPTC had longer persistence and improved effectiveness compared with emulsifiable concentrate formulations. Coffman and Gentner<sup>14</sup> found that trifluralin formulated as starch xanthide granules persisted longer than either emulsifiable concentrate or microcapsule formulations. When metribuzin was formulated with such adjuvants as ARD 54, ARD 93, and ARD 1836, a reduction in metribuzin injury to soybeans was observed, usually without reduction in sicklepod control.<sup>73</sup> At some locations, however, a significant reduction in sicklepod control occurred with the addition of 1% ARD 1836 and 5% linseed oil. The weaker control of weeds by simazine applied in combination with STAY-TEC in our experiment was probably due to the complexing of the herbicide with the polymer and the retention of the herbicide-polymer complex on or near the surface of the soil.

#### B. EFFECT OF STAY-TEC ON HERBICIDE ADSORPTION AND DESORPTION

To better understand the effect of STAY-TEC on the efficacy of the herbicides, the effect of the polymer was investigated on adsorption and desorption of the herbicides. In a preliminary experiment, the optimum concentration of STAY-TEC in the spray solution was determined to be 0.5% (data not presented). In another preliminary experiment, the length of time required for the herbicides, applied alone or in combination with the polymer, to become equilibrated between the soil and the aqueous phase of the suspension was investigated. When the herbicides were applied without the polymer to wet soil, adsorption of all four herbicides (bromacil, diuron, norflurazon, and simazine) increased rapidly within the first 4 h of shaking and then increased slowly for the next 20 h (Figure 1). When the two nonionic herbicides, diuron and norflurazon, were applied in combination with STAY-TEC, maximum adsorption did not occur until 48 h after shaking. STAY-TEC did not have a significant effect on the rate of adsorption of bromacil or simazine on wet soil (Figure 1) or on the adsorption of any of the four herbicides on dry soil (data not presented). Reports in the literature have indicated that the time required for maximum adsorption varied, perhaps

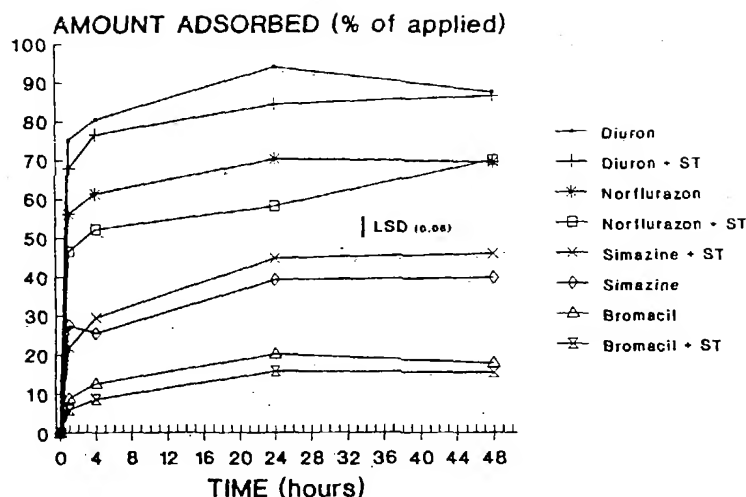


FIGURE 1. Effect of time on the adsorption of bromacil, diuron, norflurazon, and simazine applied alone or in combination with STAY-TEC.

according to herbicides and soil types. Talbert and Fletchall<sup>74</sup> indicated that adsorption of several *s*-triazines, including simazine, by soil approached equilibrium within 1 h, but continued to increase slowly with time. The small increase in adsorption with time after 1 h was thought to be due to (1) a delay in the wetting of small interior capillaries, (2) the slow diffusion of the triazines into interior surfaces, (3) a slow, irreversible fixation reaction due to chemical forces, (4) the mechanical breakage of soil particles, or (5) the formation of complexes. Carringer et al.<sup>13</sup> observed that there was no significant increase in the adsorption of several herbicides, including norflurazon, after 4 h, and Angemar et al.<sup>2</sup> observed that bromacil required a period of 24 h to attain equilibrium between soil and the aqueous phase. In all subsequent experiments using the wet soil methods, soil suspensions were shaken for 48 h, and in all experiments using the dry soil method, the suspensions were shaken for a period of 24 h.

The  $K_d$  values and the amounts of the four herbicides applied alone or in combination with STAY-TEC on wet or dry soil are presented in Table 5. Both the  $K_d$  values and the amount of herbicides adsorbed were higher on dry soil than on wet soil. The order of the extent of adsorption of the herbicides by soil colloids was diuron > norflurazon > simazine > bromacil. Addition of STAY-TEC to herbicide solutions did not result in a significant change in adsorption of the herbicides on wet soil. The addition of STAY-TEC to simazine, however, resulted in a slight increase in adsorption of the herbicide on dry soil.

The amount of bromacil adsorbed on soil colloids was desorbed almost completely with four flushes of water amounting to a total of 8 ml of elution volume (Table 6), indicating that bromacil was weakly bound to soil colloids, probably by hydrogen bonds. Weber<sup>80</sup> reported that adsorption of weakly acidic herbicides, such as dicamba, occurred by hydrogen binding. Significantly less herbicide was desorbed with 1 *N*  $\text{CaCl}_2$ . Carringer et al.<sup>13</sup> indicated that lower desorption of acidic herbicides by 1 *N*  $\text{CaCl}_2$  than by deionized water may be due to a lower solubility of the herbicide in  $\text{CaCl}_2$  than in water. There appeared to be no interaction between bromacil and STAY-TEC molecules, as no significant differences between the desorption of herbicide applied alone and that of the herbicide applied in combination with STAY-TEC were observed.

Unlike bromacil, more simazine was desorbed with 1 *N*  $\text{CaCl}_2$  than with deionized water, indicating that a cation exchange mechanism was involved in the adsorption of simazine on

TABLE 5  
Distribution Coefficient and the Amount of Herbicide Adsorbed  
When Applied Alone or with STAY-TEC on Wet or Dry Soil

Herbicide <sup>a</sup>	Wet soil		Dry soil	
	Kd (ml/g)	Amt adsorbed <sup>c</sup> (μg/g)	Kd (ml/g)	Amt adsorbed <sup>b</sup> (μg/g)
Bromacil	0.3	0.2	0.4	0.3
Bromacil + ST	0.3	0.2	0.5	0.4
Simazine	0.6	0.4	1.0 <sup>c</sup>	0.5 <sup>c</sup>
Simazine + ST	0.6	0.4	1.2 <sup>c</sup>	0.6 <sup>c</sup>
Norflurazon	2.5	0.8	3.8	0.9
Norflurazon + ST	1.7	0.7	4.1	0.9
Diuron	4.9	1.0	7.2	1.0
Diuron + ST	4.3	0.9	7.0	1.0

<sup>a</sup> STAY-TEC (ST) was added to herbicide solutions at the rate of 0.5% (v/v).

<sup>b</sup> Total amount of herbicide applied was 1.2 μg/g of soil.

<sup>c</sup> Significant at the 5% level according to the t-test.

TABLE 6  
Desorption of Adsorbed Herbicides Applied Alone or with STAY-TEC (ST) from  
Soil

Herbicide <sup>a</sup>	Desorption with d H <sub>2</sub> O (μg/g)					Desorption with 1 N CaCl <sub>2</sub> (μg/g)				
	1st	2nd	3rd	Total	%	1st	2nd	3rd	Total	%
Wet Soil										
Bromacil	0.04	0.05	0.05	0.14	76.5 <sup>b</sup>	0.05	0.04	0.03	0.12	60.0
Bromacil + ST	0.04	0.06	0.07	0.17	88.2 <sup>b</sup>	0.05	0.04	0.05	0.14	61.3
Simazine	0.15	0.10	0.05	0.30	66.7 <sup>b</sup>	0.15	0.11	0.06	0.33	71.1 <sup>b</sup>
Simazine + ST	0.14	0.09	0.04	0.27	60.0 <sup>b</sup>	0.11	0.10	0.07	0.28	64.0 <sup>b</sup>
Norflurazon	0.11	0.12	0.12	0.35	41.7	0.09	0.09	0.09	0.27	32.1
Norflurazon + ST	0.10	0.11	0.12	0.33	39.3	0.09	0.10	0.09	0.28	33.3
Diuron	0.11	0.11	0.07	0.28	29.8	0.04	0.06	0.04	0.14	15.4
Diuron + ST	0.10	0.09	0.08	0.27	28.7	0.04	0.07	0.06	0.17	18.0
Dry Soil										
Bromacil	0.07	0.07	0.07	0.21	72.4	0.07	0.06	0.06	0.19	65.5
Bromacil + ST	0.08	0.06	0.06	0.20	69.0	0.08	0.07	0.06	0.21	70.4
Simazine	0.13	0.10	0.07	0.30	50.3 <sup>b</sup>	0.13	0.10	0.08	0.31	57.3 <sup>b</sup>
Simazine + ST	0.13	0.08	0.07	0.28	42.4 <sup>b</sup>	0.13	0.09	0.07	0.29	45.9 <sup>b</sup>
Norflurazon	0.13	0.10	0.09	0.32	32.2	0.08	0.09	0.08	0.25	25.8
Norflurazon + ST	0.11	0.10	0.09	0.30	31.1	0.07	0.07	0.07	0.21	22.0
Diuron	0.09	0.09	0.07	0.25	24.7	0.06	0.06	0.05	0.16	18.4
Diuron + ST	0.09	0.07	0.06	0.22	20.2	0.06	0.06	0.05	0.17	17.4

<sup>a</sup> STAY-TEC (ST) was added to herbicide solutions at the rate of 0.5% (v/v).

<sup>b</sup> Significant at the 5% level according to the t-test.



soil colloids. These results are in agreement with those of Carringer et al.<sup>13</sup> who reported that basic herbicides, such as prometryn, were desorbed much more by 1*N* CaCl<sub>2</sub> than by water. It is also interesting to note that more simazine was desorbed when it was applied alone than when it was applied in combination with STAY-TEC, indicating that a weak interaction between simazine and STAY-TEC molecules may have occurred, which might have changed the mechanism, or the strength, of adsorption of the herbicide on soil colloids. The mechanism of adsorption of STAY-TEC on soil colloids is not known.

Norflurazon and diuron are nonionic herbicides that showed a similar pattern of desorption from soil colloids. Norflurazon, with a slightly lower partition coefficient, was desorbed more easily with deionized water than with 1*N* CaCl<sub>2</sub>. It has been suggested that the adsorption mechanism of nonionic herbicides was due primarily to hydrophobic association of the organic molecules with the soil organic-matter surface and that the less soluble compounds were also less easily desorbed from the soil.<sup>13</sup> Slightly more norflurazon was desorbed with water when the herbicide was applied alone than when it was applied in combination with STAY-TEC, suggesting some interaction of the herbicide with the polymer molecules. No such interaction was apparent in the case of diuron.

### C. EFFECT OF STAY-TEC ON HERBICIDE MOBILITY

The mobility of herbicides applied alone or in combination with STAY-TEC was studied using soil TLC. Bromacil was most mobile, whereas, diuron was least mobile on soil TLC plates (Figures 2A and 2B). There was no significant difference in the mobility of the herbicides when they were applied alone and in combination with STAY-TEC. Simazine was less mobile than bromacil, but more mobile than diuron. When applied alone, simazine was distributed almost evenly in the first 8 cm of the plate (Figure 2D). When applied in combination with STAY-TEC, however, much more simazine was retained at the point of application than when the herbicide was applied alone. These results are similar to those of Street et al.,<sup>73</sup> who reported that certain cationic surfactants reduced slightly the movement of metribuzin on soil TLC plates. Norflurazon was less mobile than bromacil or simazine (Figure 2C). STAY-TEC reduced the mobility of norflurazon on soil TLC plates, but to a much lesser extent than that of simazine (Figure 2D).

The mobility of herbicides applied alone or in combination with STAY-TEC was also studied using soil leaching columns. As observed with the soil TLC plates, bromacil was most mobile and diuron was least mobile in soil leaching columns (Figures 3A and 3B). The mobility of either herbicide was not affected by the addition of STAY-TEC to the herbicide solutions.

Simazine was less mobile than bromacil in soil leaching columns (Figure 3D). When it was applied with STAY-TEC, significantly more herbicide was retained in the top 5 cm of the columns than when the herbicide was applied alone, thus confirming the results of the soil TLC plates.

Norflurazon was much less mobile in soils than bromacil or simazine, but it was slightly more mobile than diuron (Figure 3C). Contrary to the results obtained with the soil TLC plates, however, no differences were observed between the mobility of norflurazon applied alone and that of the herbicide applied in combination with STAY-TEC.

## IV. SUMMARY AND CONCLUSIONS

Adsorption and leaching are two of the most important physicochemical factors that affect herbicide efficacy in soil. Besides reducing herbicide efficacy, low adsorption and high leaching of chemicals in the soil can cause groundwater contamination. The use of certain adjuvants offers the opportunity to increase the efficacy of herbicides in the soil by



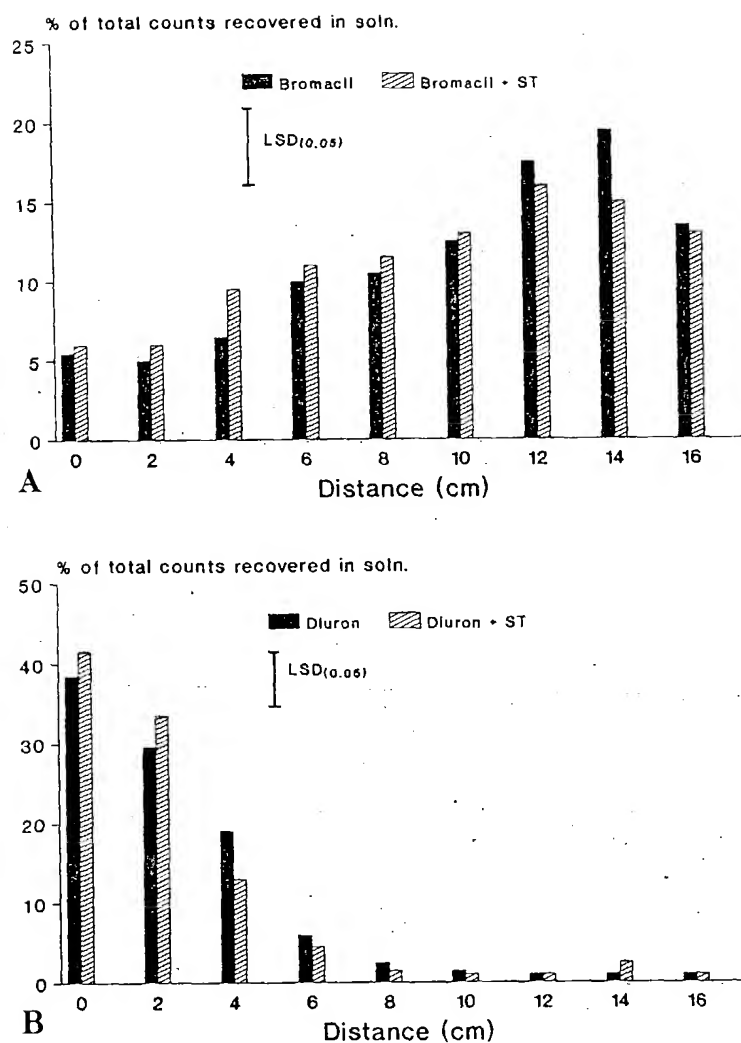


FIGURE 2. Mobility of (A) bromacil, (B) diuron, (C) norflurazon, and (D) simazine applied alone and in combination with STAY-TEC on a soil thin-layer chromatography plate.

reducing their leaching losses. STAY-TEC, when added to herbicide solutions, increased the efficacy of bromacil, norflurazon, and simazine, which provided longer lasting weed control in the field than the herbicides applied without STAY-TEC. In greenhouse experiments, simazine applied with STAY-TEC provided less control of weeds than the herbicide applied alone in the first 6 weeks after application. Herbicidal activity was higher, however, in trays treated with simazine applied in combination with STAY-TEC than in trays treated with simazine alone 12 weeks after treatment. In laboratory experiments, STAY-TEC increased the adsorption and decreased the mobility of simazine, but it did not affect the adsorption or leaching of bromacil, norflurazon, or diuron in soil. As seen from the greenhouse experiment, one problem with controlled-release formulations is that the amount of herbicide released from the herbicide-polymer complex initially is not sufficient to provide effective weed control. Therefore, the rates of the herbicides should be adjusted to provide concentrations high enough for weed control, but well below the tolerance level of the

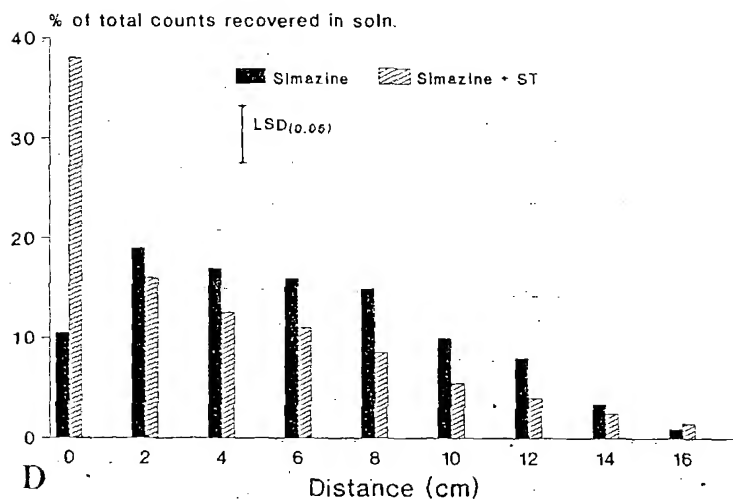
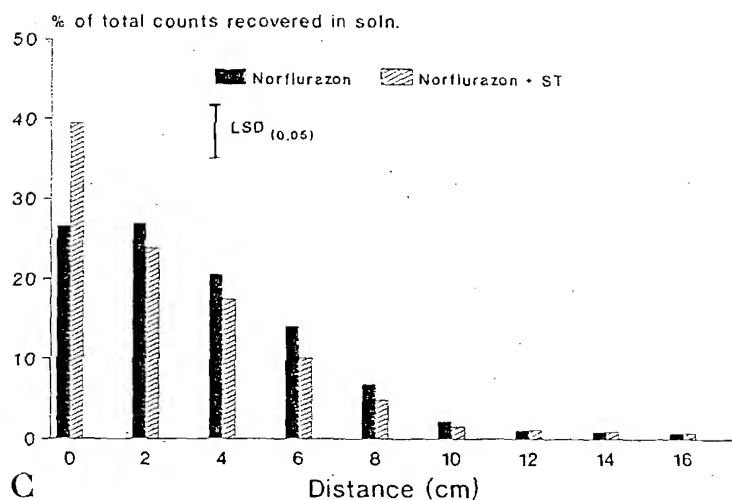


FIGURE 2 (continued).

associated crop. Successful release of the herbicide from the herbicide-polymer complex in desired concentrations will depend upon several factors, such as rainfall, pH, soil type, etc. The polymers used as controlled-release agents should be biodegradable and should not alter the soil physical characteristics permanently. Nevertheless, in view of the increasing public concern with groundwater contamination from pesticides, controlled release of herbicides with polymers holds considerable promise for improving the efficacy of herbicides and reducing their leaching in soil.

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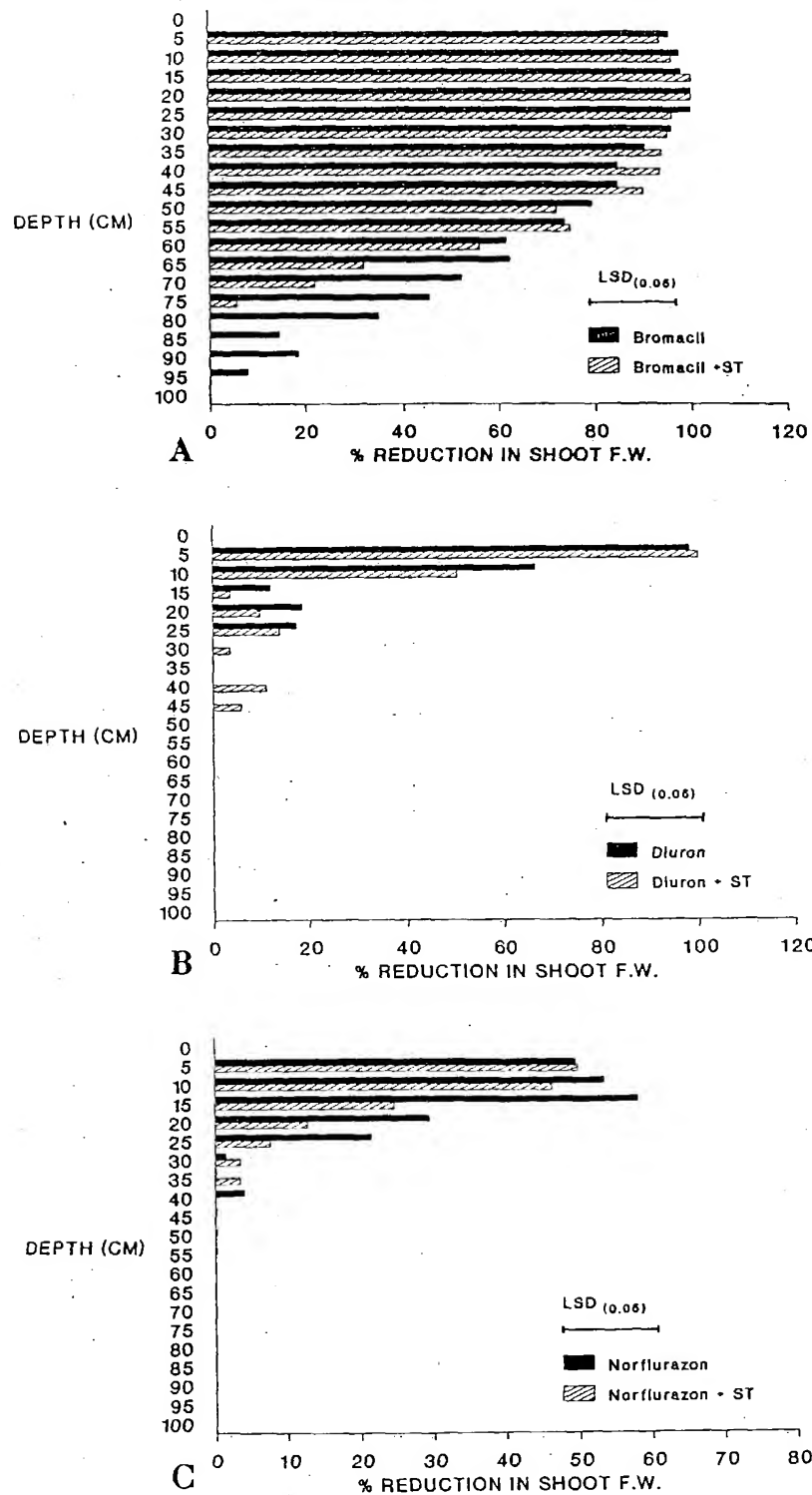


FIGURE 3. Effect of STAY-TEC on mobility of (A) bromacil, (B) diuron, (C) norflurazon, and (D) simazine in soil leaching columns.

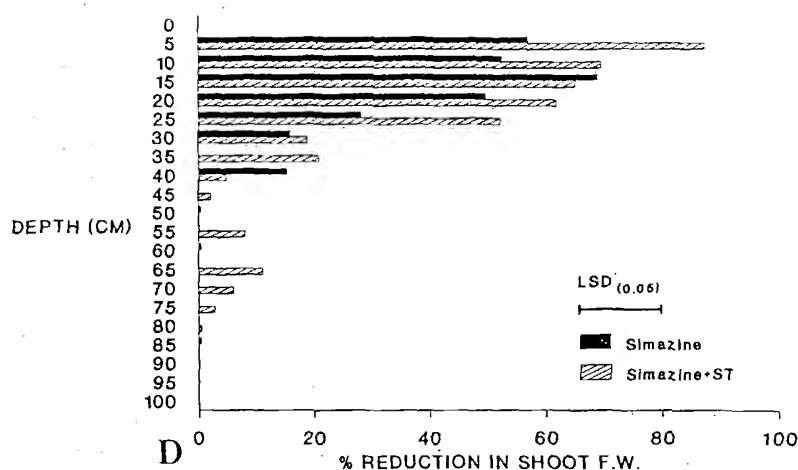


FIGURE 3 (continued).

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## Chapter 33

**INFLUENCE OF CERTAIN SURFACTANTS ON THE MOBILITY  
OF SELECTED HERBICIDES IN SOIL**

Chester L. Foy

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## ABSTRACT

Two procedures were employed to study the effects of various adjuvants on the leaching of selected herbicides in soil: (1) percolation through soil columns and (2) soil thin-layer chromatography (TLC). The relative leachabilities of dicamba (highly mobile), atrazine (intermediate), and chlorpropham or trifluralin (relatively immobile) were confirmed in both systems. Certain surfactants, at high rates, markedly enhanced herbicide mobility. Even chlorpropham and trifluralin were leachable under appropriate conditions. However, the anionic, nonionic, and cationic surfactants tested caused variable effects on water movement and herbicide movement, depending on the herbicide, surfactant, dosage or concentration, soil type, and preleaching conditions. Generally, the herbicides were less mobile in a Dismal Swamp organic soil (80% organic matter) than in Norfolk sandy loam.

## I. INTRODUCTION

Herbicides are now used extensively as "prescription tools" in technologically advanced agriculture. Public concern over pollution of the environment has also increased. Therefore, better manipulation and control of the distribution and fate of herbicides in the biosphere is desirable. Herbicide mobility in the soil profile is important because of its possible influence on weed control efficacy, herbicidal selectivity, herbicide dissipation, persistence of chemical residues potentially harmful to succeeding crops, and contamination of soil, water, air, or food (feed) crops, perhaps beyond acceptable tolerance levels.

Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] is a widely used selective herbicide. Postemergence applications are usually made with a nonphytotoxic crop oil, crop oil concentrate, or surfactant.<sup>10</sup> Movement or leaching of atrazine is limited by its adsorption to certain soil constituents; however, adsorption is reversible and desorption often occurs readily, depending on such factors as temperature, moisture, and pH. Atrazine normally is not found below the upper 30 cm of soil in detectable quantities, even after years of continuous use.

Chlorpropham (1-methylethyl-3-chlorophenylcarbamate) is a highly selective herbicide and is adsorbed readily to organic matter in soil.<sup>10</sup> Thus, the organic matter content of soil is the major controlling factor in influencing the degree of leaching which occurs.

Dicamba (3,6-dichloro-2-methoxybenzoic acid) controls broadleaf weeds in selected crops, turf, pasture, rangeland, and noncrop land, and brush and vines in pasture, rangeland, and noncrop areas. Dicamba is relatively mobile in soil, and maximum leaching occurs with larger total quantities of liquid or smaller increments of equal leaching totals.<sup>10</sup>

Trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine] is registered for use in numerous crops. Trifluralin is strongly adsorbed on soil and shows negligible leaching.<sup>10</sup>

As reported by Weber et al.,<sup>9</sup> the relative mobility of selected herbicides has been determined by using soil leaching columns and soil TLC. Several studies involving the use of adjuvants on or in soil have been conducted; however, information concerning the effects of adjuvants on the movement of herbicides is limited.<sup>2</sup> Bayer<sup>1</sup> reported diverse effects of surfactants on the movement of substituted urea herbicides in soil. The surfactants used caused both increases and reductions in the leaching of herbicides. Several surfactants decreased the amount of diuron [*N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea] adsorbed by the soil.<sup>1,4</sup>

Emulsifiers formulated onto granules with triallate [*S*-(2,3,3-trichloro-2-propenyl)bis(1-methylethyl)carbamothioate] resulted in enhanced movement of the herbicide through Drummer soil (9% sand, 55% silt, 36% clay, and 12% organic matter) in response to 15.2 cm of rainfall.<sup>3</sup> Without emulsifiers, 95% of the recovered triallate was in the upper centimeters



of the soil. With emulsifiers, four times more triallate was moved beyond 1 cm, but movement was not extensive (3 cm).

A synthetic polymer, STAY-TEC® (Delacar Corp., Tavares, FL), reduced the mobility of simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine) on soil TLC plates and in soil leaching columns.<sup>7</sup> The polymer at 5% (v/v) added to simazine solutions increased slightly the amount of simazine adsorbed on soil colloids and decreased the rate of desorption of the herbicide. The polymer did not affect the adsorption to soil colloids or mobility of bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1*H*,3*H*)pyrimidinedione], norflurazon [4-chloro-5-(methylamino)-2-(3-trifluoromethyl)phenyl]-3(2*H*)-pyridazinone], or diuron.

Surfactants added to a solution of trifluralin or oryzalin at 2% of the spray volume increased the depth of both water penetration and herbicide movement in soil.<sup>8</sup> Trifluralin movement in dry soil was less than in prewetted soil when no surfactants were added. However, surfactants had a greater influence in leaching of this herbicide in dry soil than in wet soil, although leaching was increased in both.

The purpose of this work was to evaluate the effects of various surfactants and other adjuvants on the mobility of atrazine, chlorpropham, dicamba, and trifluralin in soils.

## II. MATERIALS AND METHODS

### A. LEACHING COLUMN EXPERIMENTS

Conventional leaching columns 50 cm long were constructed of 4.4-cm I.D. solvent-weld plastic pipe which had been precut into 5-cm sections. Columns were packed with 1300 to 1400 g of air-dried Norfolk sandy loam soil, and atrazine, dicamba, or trifluralin was applied to the surface at the rate of 8.96 kg ha<sup>-1</sup> in 3 ml of water, or no herbicide was applied, and then leached with water or solutions of 1000, 10,000, and 100,000 ppm (v/v) Tween 80 nonionic surfactant equivalent to 5, 10, or 20 cm of rainfall. A second set of columns was packed but leached with water prior to herbicide treatment and then leached with the same concentrations of Tween 80 as above. A third set of columns was packed with soil previously coated with 0.1, 1.0, 10.0, or 100.0 ppm Tween 80 (vol/dry wt basis), the herbicides were applied, and the columns were then leached with water. All treatments were replicated four times. A head of water was maintained on the columns until all the leach solution was added. The columns were sectioned and the soil from each 5-cm section was placed in a 145-ml cup. Eight oat (*Avena sativa* L.) seeds were planted in each cup in the greenhouse. Plants were harvested 3 weeks after planting and dry weights were recorded.

In the columns that were leached with the equivalent of 20 cm of water, the leachate was collected from each column and used to water four 145-ml cups planted with oats as described above.

### B. SOIL THIN-LAYER CHROMATOGRAPHY

Soil TLC procedures described by Helling<sup>5</sup> and Helling and Turner<sup>6</sup> were followed. Norfolk sandy loam soil and Dismal Swamp organic soil (80% organic matter) were air dried and sifted through a 40-mesh screen. Water was added to the soils to make a slurry which was spread evenly on glass plates. This was achieved by placing masking tape along the plate edges and moving a glass rod over the slurry. Soils on the glass plates were allowed to dry for 24 h and then spotted with <sup>14</sup>C-labeled dicamba, atrazine, or chlorpropham. Plates were developed at least 10 cm with 0, 0.1, 1.0, and 10% Tween 80® solutions by ascending chromatography in one experiment. In a second experiment, Dismal Swamp organic soil was precoated with various concentrations of Tween 80 (nonionic surfactant), Hyamine 1622 (cationic surfactant), sodium lauryl sulfate (anionic surfactant), Sun 11E (paraffinic phytobland oil), and Sun 100E (naphthenic phytobland oil). The two phytobland oils were also



compared to Rohm and Haas 9D-207 emulsifier, since the oils contained 2% (v/v) of 9D-207. The soil was precoated with various concentrations of the surfactant, phytobland oil, or emulsifier prior to plating. After the soils were allowed to dry for 24 h,  $^{14}\text{C}$ -labeled dicamba, atrazine, or chlorpropham was spotted on the plates and developed with water by ascending chromatography. Distribution patterns were determined by autoradiography and counting at different  $R_f$  positions.

### III. RESULTS AND DISCUSSION

#### A. LEACHING COLUMN EXPERIMENTS

Atrazine was distributed throughout the upper 20 cm in the soil columns which received no pretreatment and were leached with water equal to 5 cm of rainfall (Figure 1). When the columns were leached with solutions of Tween 80, atrazine was distributed in the upper 25 to 35 cm. Atrazine was distributed throughout 25 to 30 cm when the columns were leached with Tween 80 at 0, 1000, and 10,000 ppm and throughout 50 cm with Tween 80 at 100,000 ppm in the equivalent of 10 cm of rainfall (Figure 1).

Atrazine exhibited a somewhat uniform distribution throughout the soil columns when the columns were preleached with water prior to the application of the herbicide and leach solutions (Figure 2). Tween 80 at 0.1, 1.0, 10.0, and 100.0 ppm mixed with the soil prior to packing the columns resulted in atrazine movement throughout the upper 20 to 25 cm of the column when leached with water equal to 5 cm of rainfall (Figure 3). Atrazine movement was 25 cm with Tween 80 at 0.1 ppm, 30 cm with Tween 80 at 1.0 and 10.0 ppm, and 35 cm with Tween 80 at 100.0 ppm mixed with the soil and leached with water equal to 10 cm of rainfall (Figure 3).

Atrazine was distributed evenly throughout the columns in all cases when leached with water or Tween 80 at all concentrations equal to 20 cm of rainfall (Figures 1 through 3).

Tween 80 at 1000, 10,000, and 100,000 ppm in the equivalent of 5 cm of rainfall moved dicamba approximately 35 cm, compared to 30 cm with water alone in the soil columns which received no pretreatment (Figure 4). Leaching with water or Tween 80 solutions equal to 10 cm of rainfall resulted in dicamba movement throughout the column. Leach solutions of water or Tween 80 at 1000 and 10,000 ppm equal to 20 cm of rainfall resulted in growth reductions of the bioassay crop in the lower portions of the columns (Figure 4). High concentrations of dicamba remained throughout the column with Tween 80 at 100,000 ppm.

Similar trends in the movement of dicamba were observed when columns were preleached with water or when Tween 80 was mixed with the soil prior to packing the columns (Figures 5 and 6). Increased movement was observed as rainfall amounts increased. When the columns were preleached with water, concentrations of dicamba appeared to be higher in the 0- to 35-cm portion of the columns leached with water (10-cm rainfall equivalent) than with Tween 80 at all concentrations (Figure 5).

Trifluralin was concentrated in the upper 15 cm when the columns were leached with water equal to 5 cm of rainfall in columns that were not pretreated (Figure 7). Tween 80 at 1000, 10,000, and 100,000 ppm increased the movement of trifluralin by 10, 30, and 30 cm, respectively. Results varied somewhat when the columns were leached with the equivalent of 10 cm of rainfall, particularly with water alone (Figure 7). Tween 80 increased the movement of trifluralin throughout the column. Leaching with the equivalent of 20 cm of rainfall or Tween 80 at 10,000 or 100,000 ppm moved trifluralin throughout the column (Figure 7). Trifluralin was less mobile with Tween 80 at 1000 ppm.

Preleaching the soil columns with water resulted in trifluralin movement throughout the columns when leached with 5, 10, or 20 cm rainfall equivalent or with Tween 80 at 0, 1000, 10,000, and 100,000 ppm (Figure 8).

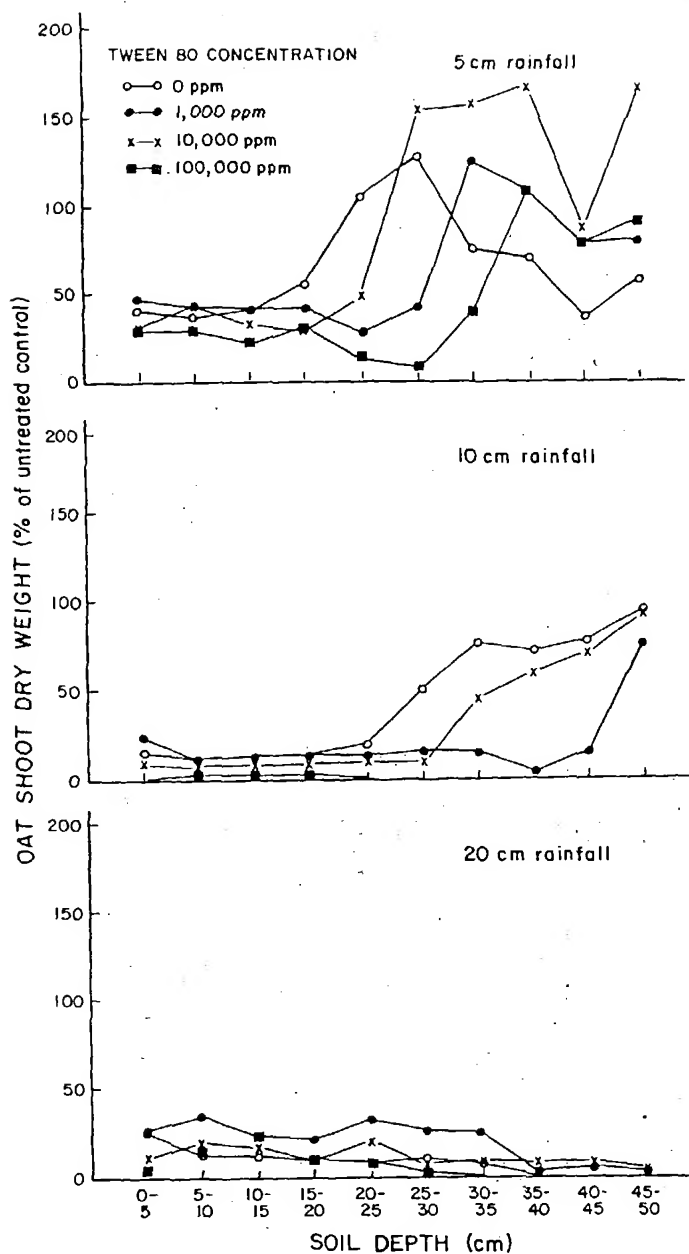


FIGURE 1. The effect of Tween 80 in leach solutions equal to 5, 10, or 20 cm of rainfall on the mobility of atrazine in Norfolk sandy loam soil with no pretreatment.

Tween 80 mixed with the soil did not affect the movement of trifluralin when leached with water equal to 5 cm of rainfall (Figure 9). Leaching with the equivalent of 10 or 20 cm of rainfall moved trifluralin throughout the columns. The highest concentrations of trifluralin were in the 20- to 50-cm sections when leached with the equivalent of 20 cm of rainfall (Figure 9).

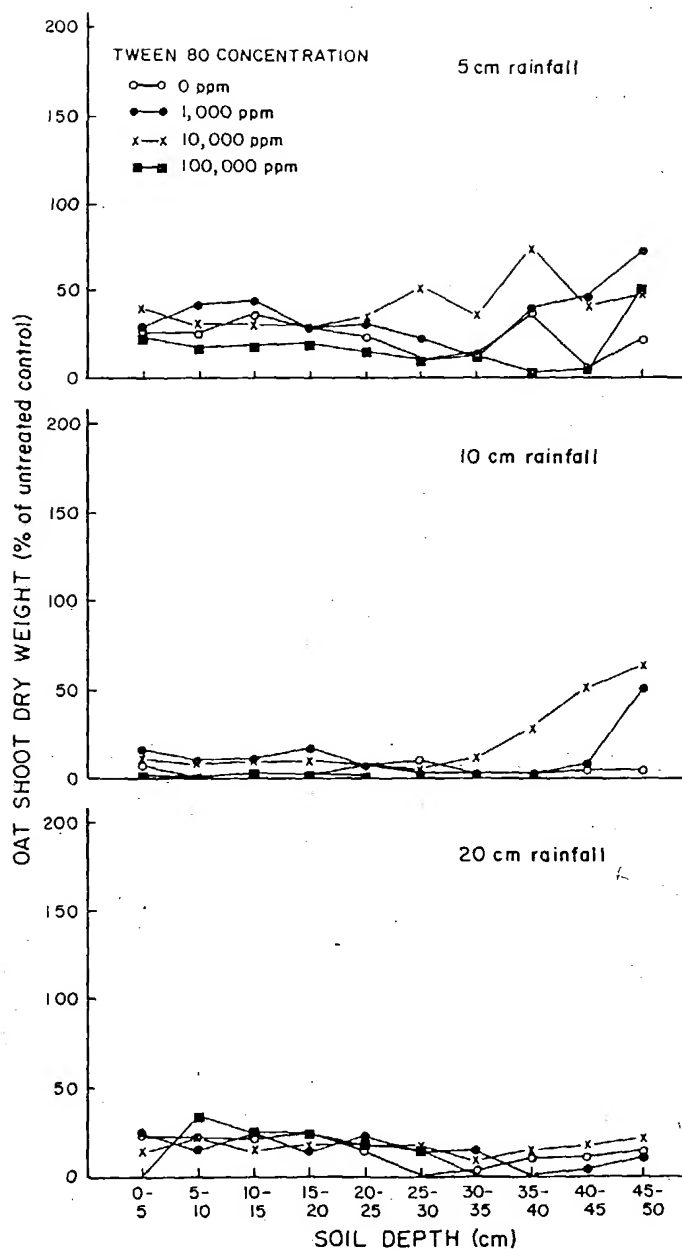


FIGURE 2. The effect of Tween 80 in leach solutions equal to 5, 10, or 20 cm of rainfall on the mobility of atrazine in Norfolk sandy loam soil preleached with water.

The highest concentrations of atrazine in the leachates collected from columns leached with the equivalent of 20 cm of rainfall (water or Tween 80) were from columns which were preleached with water (Figure 10). High concentrations were also found in columns which received no pretreatment, and these concentrations increased as the concentrations of Tween 80 increased. Results with atrazine varied when Tween 80 was mixed with the soil and leached with water (Figure 11).

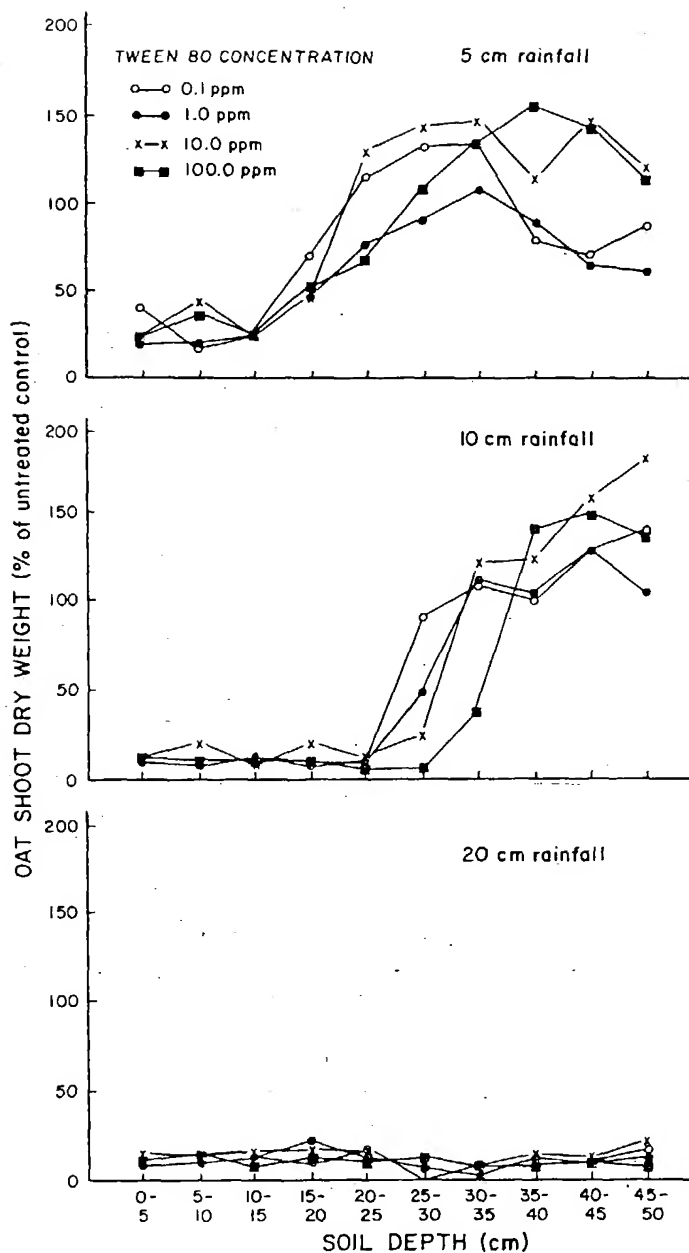


FIGURE 3. The effect of Tween 80 mixed with air-dry Norfolk sandy loam soil prior to packing the columns on the mobility of atrazine. Columns were leached with water equal to 5, 10, or 20 cm of rainfall.

High concentrations of dicamba were present in the leachates collected from all columns leached with the equivalent of 20 cm of rainfall (Figures 10 and 11). High concentrations of trifluralin were present in leachates collected from columns which were not pretreated and leached with Tween 80 at 100,000 ppm (Figure 10). When the columns were preleached, high concentrations of trifluralin were present in leachates from columns leached with Tween 80 at 10,000 and 100,000 ppm. No adverse effects on oat shoot growth occurred with trifluralin when Tween 80 was mixed with the soil and leached with water (Figure 11).

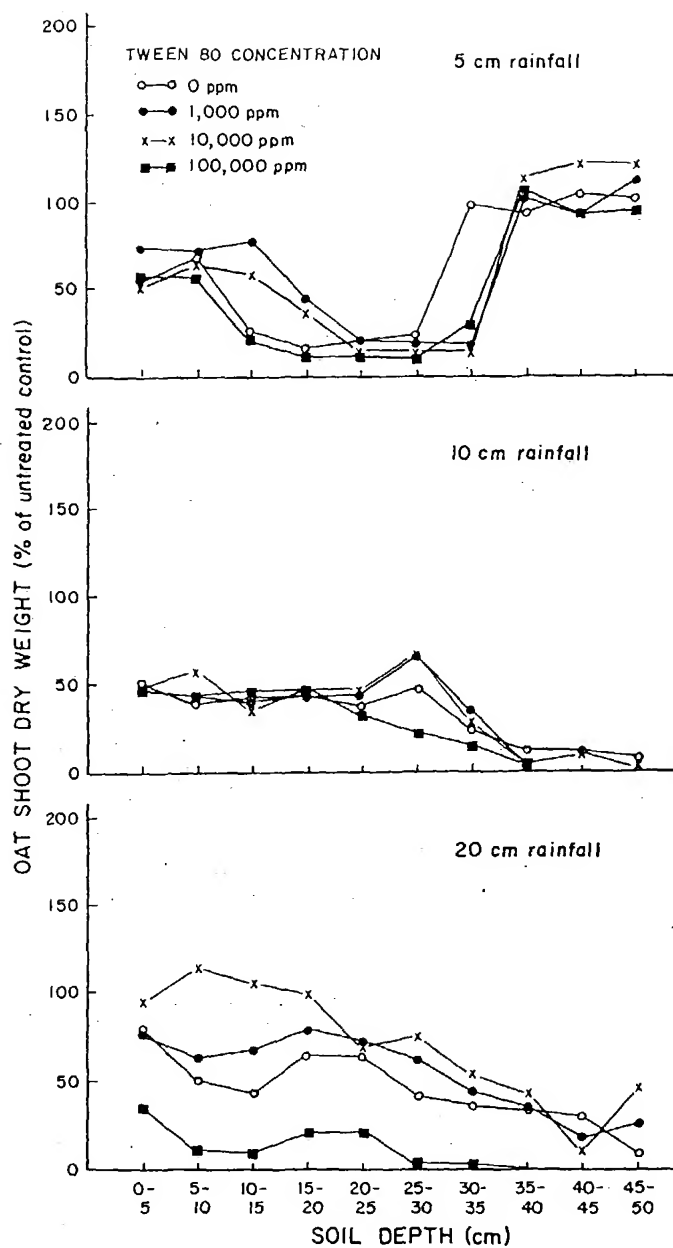


FIGURE 4. The effect of Tween 80 in leach solutions equal to 5, 10, or 20 cm of rainfall on the mobility of dicamba in Norfolk sandy loam soil with no pretreatment.

#### B. SOIL THIN-LAYER CHROMATOGRAPHY

Tween 80 at 0.1, 1.0, and 10.0% in the developing solvent clearly increased the movement of atrazine and chlorpropham in Norfolk sandy loam soil (Figure 12). No effect of Tween 80 on the movement of dicamba was apparent because dicamba moved freely in water alone.

In general, the herbicides were less mobile in Dismal Swamp organic soil than in Norfolk sandy loam soil (Figure 12). Using water alone or a 0.1% solution of Tween 80 as the



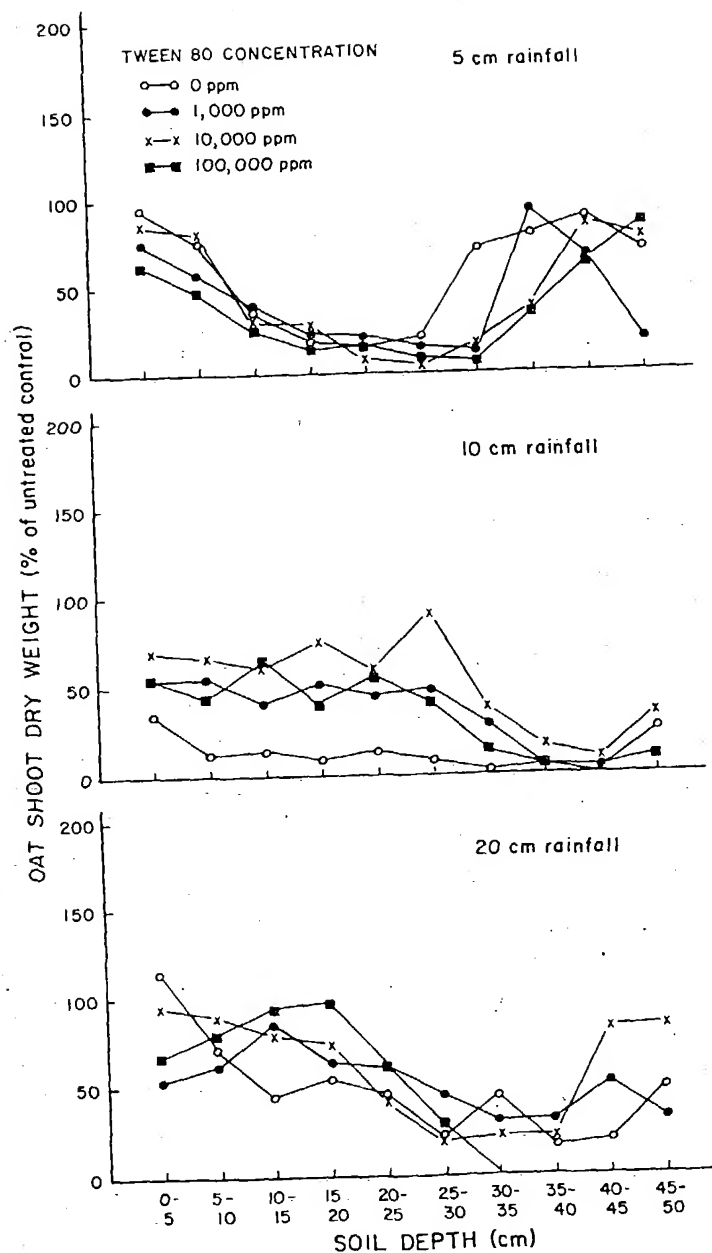


FIGURE 5. The effect of Tween 80 in leach solutions equal to 5, 10, or 20 cm of rainfall on the mobility of dicamba in Norfolk sandy loam soil preleached with water.

developing solvent, the order of mobility in the organic soil was dicamba > atrazine > chlorpropham. With 1.0% Tween 80, the order of mobility was dicamba > chlorpropham > atrazine (Figure 12). However, with Tween 80 at 10%, chlorpropham became the most mobile, followed by dicamba and atrazine.

In a second experiment where Dismal Swamp organic soil was precoated with the adjuvants and soil TLC plates were developed with water, sodium lauryl sulfate, Hyamine

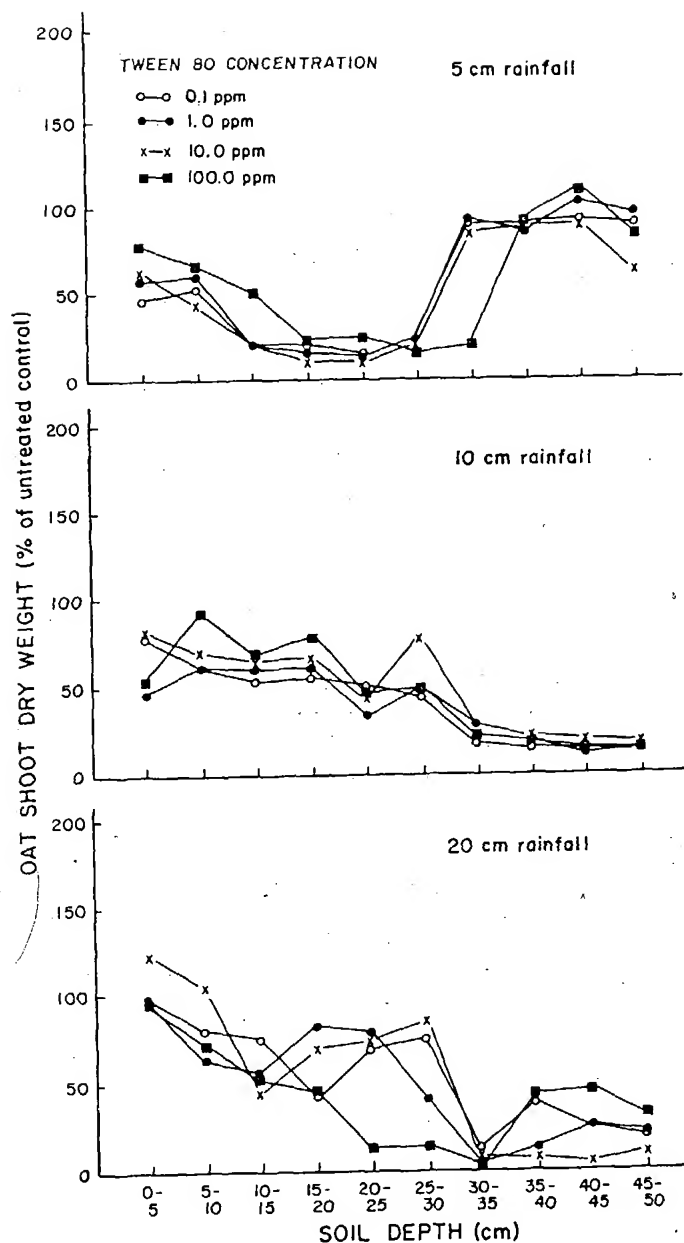


FIGURE 6. The effect of Tween 80 mixed with air-dry Norfolk sandy loam soil prior to packing the columns on the mobility of dicamba. Columns were leached with water equal to 5, 10, or 20 cm of rainfall.

1622, and Tween 80 caused variable effects on herbicide movement (Figure 13). The order of mobility was dicamba > atrazine > chlorpropham, except with cationic Hyamine 1622 at 100,000 ppm (atrazine > chlorpropham > dicamba). The mobility of atrazine was increased only by the highest concentration (100,000 ppm) of the surfactants (Figure 13). The mobility of chlorpropham was affected differentially, but only at higher concentrations of the surfactants.

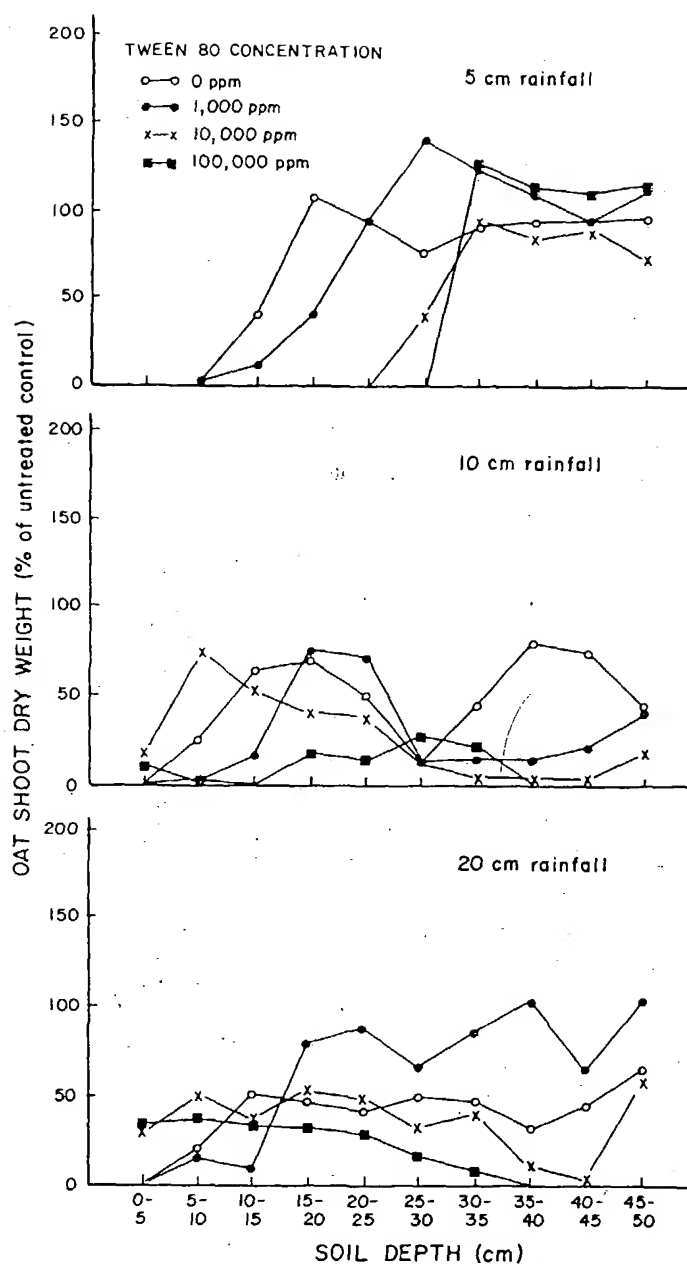


FIGURE 7. The effect of Tween 80 in leach solutions equal to 5, 10, or 20 cm of rainfall on the mobility of trifluralin in Norfolk sandy loam soil with no pretreatment.

Sun 11E, Sun 100E, and Rohm and Haas 9D-207 emulsifier had little or no effect on the movement of atrazine and chlorpropham in the organic soil (Figure 14). Slight increases on the movement of dicamba were observed.

The behavior of surfactants in soil is not fully understood, but they must influence the physicochemical aspects of the soil as well as the herbicide.<sup>2</sup> The influence of the surfactant on the soil properties undoubtedly is more important than the solvent effects of the surfactant

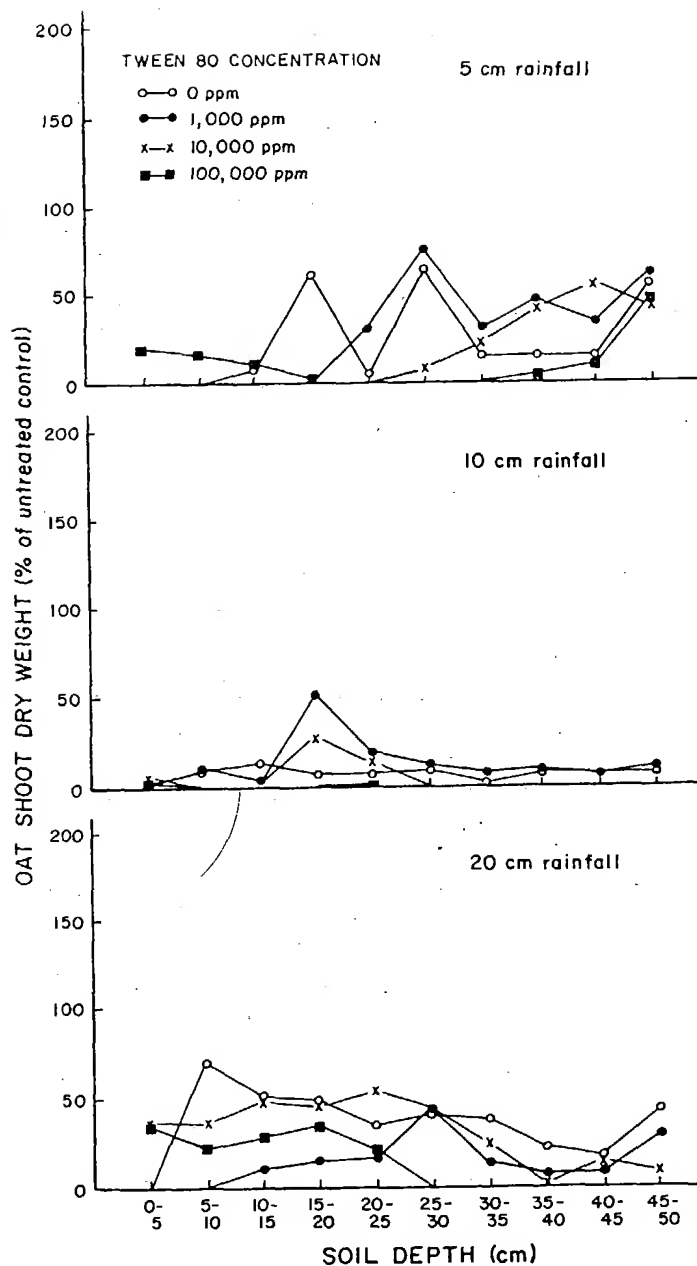


FIGURE 8. The effect of Tween 80 in leach solutions equal to 5, 10, or 20 cm of rainfall on the mobility of trifluralin in Norfolk sandy loam soil preleached with water.

on the herbicide in determining the rate and depth of leaching of the herbicide. Low dosages of surfactants which would result from normal spray additive concentrations applied in the field appeared to have little or no effect on the distributional fate of herbicides in soil profiles following irrigation. Conceivably, however, intentionally higher levels of surfactant might be used to enhance or retard the movement of both herbicides and water in soils, according to design and purpose.

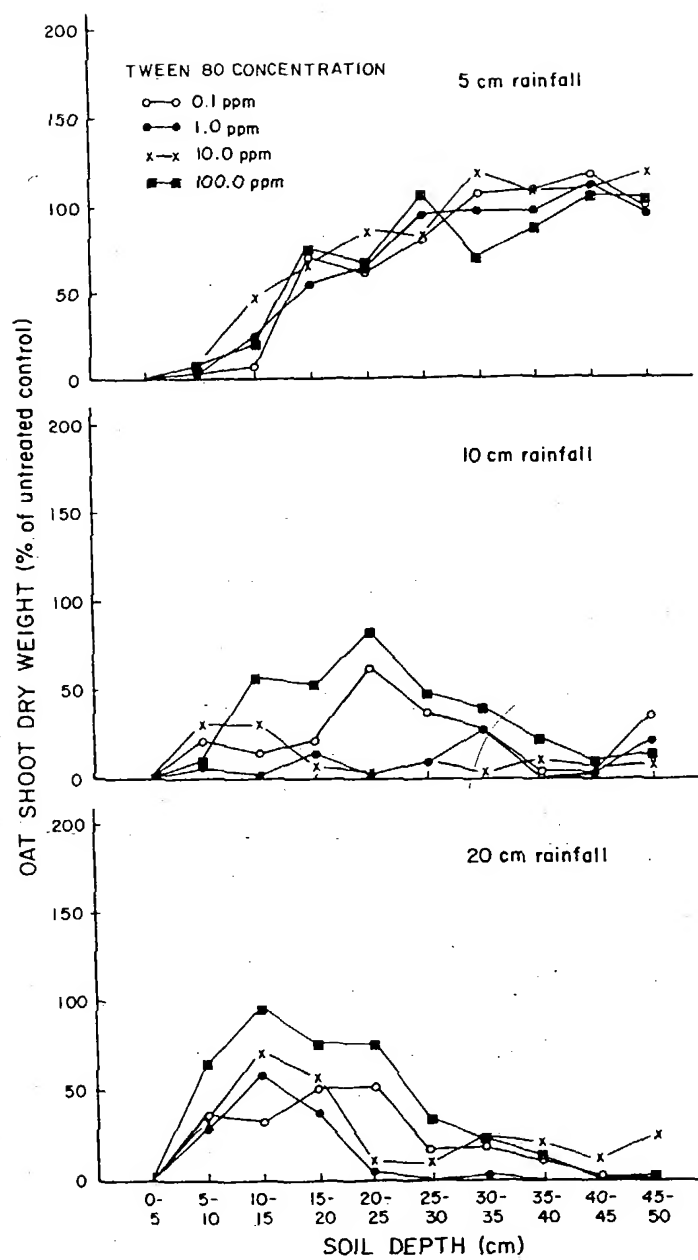


FIGURE 9. The effect of Tween 80 mixed with air-dry Norfolk sandy loam soil prior to packing the columns on the mobility of trifluralin. Columns were leached with water equal to 5, 10, or 20 cm of rainfall.



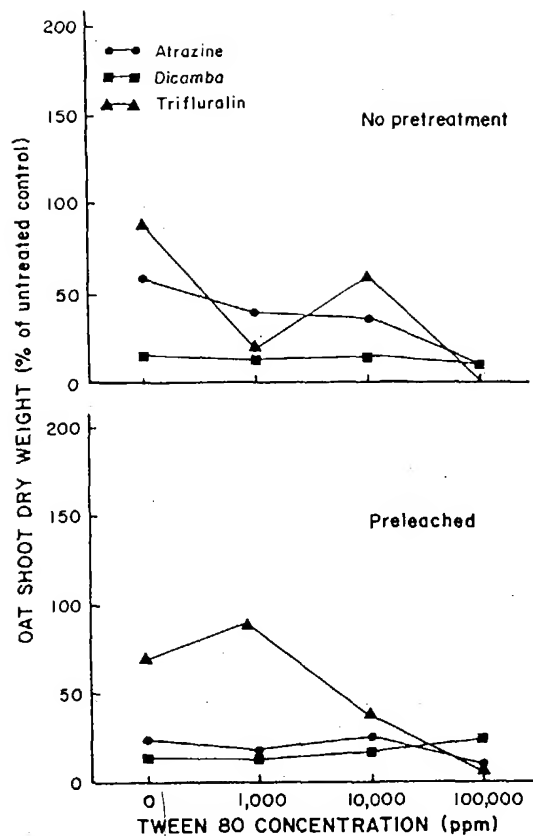


FIGURE 10. The effect of leachates collected from columns which received the equivalent of 20 cm of rainfall and used to water cups planted to oats on the shoot growth of oats. Columns received no pretreatment or were preleached with water prior to the application of the herbicides and leach solutions.

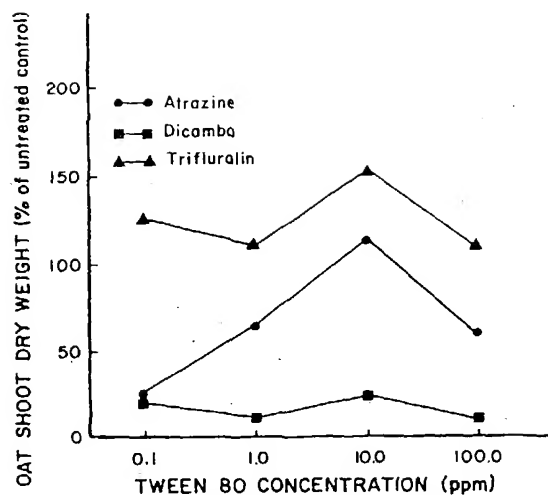


FIGURE 11. The effect of leachates collected from columns which received the equivalent of 20 cm of rainfall and used to water cups planted to oats on the shoot growth of oats. Tween 80 was mixed with air-dry Norfolk sandy loam soil prior to packing the columns.

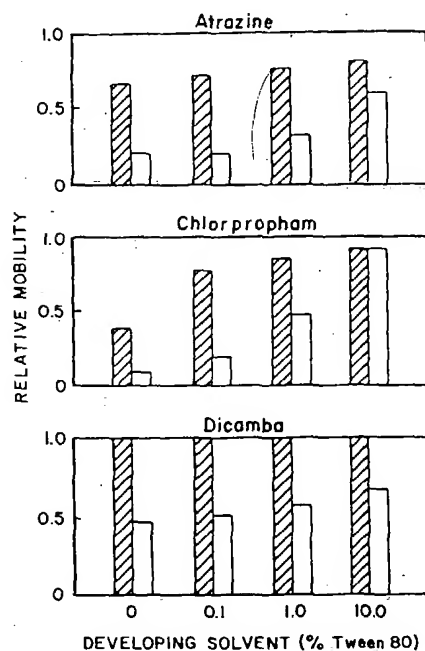


FIGURE 12. The effect of Tween 80 on the mobility of atrazine, chlorpropham, and dicamba in Norfolk sandy loam soil (hatched) and Dismal Swamp organic soil (white) using TLC plates.

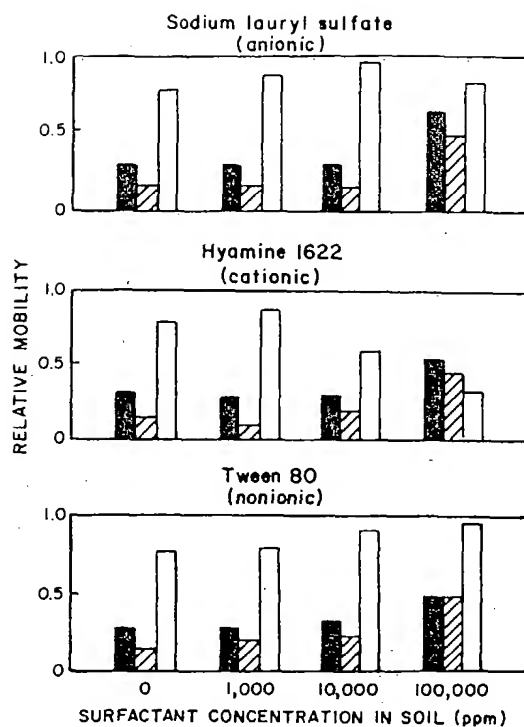


FIGURE 13. The effect of surfactants mixed with Dismal Swamp organic soil on the mobility of atrazine (■), chlorpropham (▨), and dicamba (□) on soil TLC plates. Plates were developed with water.

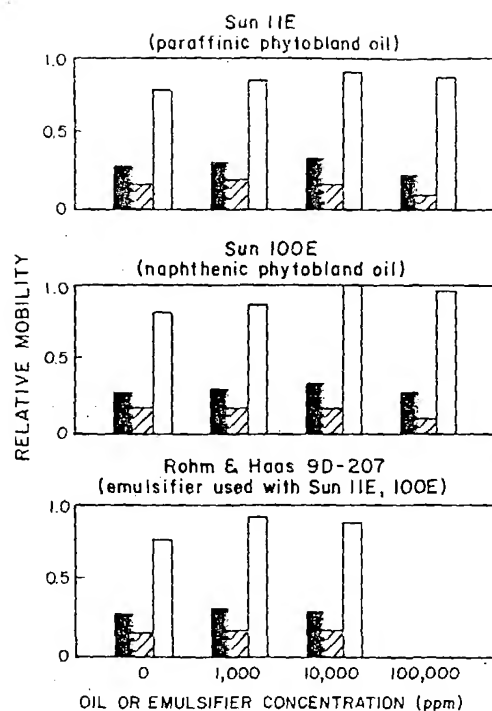


FIGURE 14. The effect of two oils and an emulsifier mixed with Dismal Swamp organic soil on the mobility of atrazine (■), chlorpropham (▨), and dicamba (□) on soil TLC plates. Plates were developed with water.

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## Chapter 34

**ACA-160, A NEW CLASS OF WETTING AGENTS FOR SOILLESS MIXES**

A. R. Templeton and D. A. Rodriguez

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## ABSTRACT

The need for wetting agents in soilless mixes has been recognized for some time. This need is based on the extreme hydrophobicity of peat, which is a common component of such mixes. ACA-160 represents a new class of wetting agents which have been specifically designed and selected for this purpose. This new chemistry has superior wetting properties, improved crop safety, and better storage performance than the industry standard.

## I. INTRODUCTION

Surfactants, or wetting agents, have been used to treat a variety of organic or synthetic plant-growing media for a number of years.<sup>1,3</sup> Although in wide use, little attention has been given to developing new and improved products which address the specific needs of commercial growers. Materials currently in use may cause problems in germination and seedling growth if used improperly. As synthetic media, particularly peat-lite mixes, dry, they become extremely difficult to wet. Surfactants also biodegrade once in use and reapplication is needed. Upon reapplication, they may come into contact with plant foliage. Therefore, a need exists to identify new chemistry which has improved crop safety, better rewetting at low moisture levels, may be used at lower rates to reduce environmental concerns, does not injure plant foliage, and is more economical.

## II. MATERIALS AND METHODS

To date, we have evaluated over 300 surfactants for their ability to wet peat and peat-lite mixes. The most important criterion for selection, however, is their safety for crops. For the purposes of this study, data for AquaGro® (Aquatrols Corporation of America, Pennsauken, NJ 08110), the industry standard, are included for comparative purposes. To determine the relative ease of wetting of surfactants, solutions giving the equivalent of rates ranging from 40 to 350 ml/m<sup>3</sup> were prepared and 90 ml introduced into a petri dish, after which a compressed peat pellet was placed in each dish. Treatments were replicated five times at each concentration and the time to fully hydrate the peat pellet was measured.

To determine crop safety, 14-dm<sup>3</sup> samples using ACA-160 and AquaGro were prepared using a known "hard to wet" mix. The two surfactants were introduced at the appropriate concentration in 2 l of distilled water, thoroughly incorporated, and left to stand for 24 h to insure even distribution. Samples were given to a commercial grower for evaluation and were also tested in our own laboratories. The treated mixes, as well as a control containing no wetting agents, were placed in plug trays. Seeds of hybrid *Impatiens* sp. (cv. Gem White); marigold (*Tagetes erecta*, cv. Dwarf French Bonanza), *Begonia* sp. (cv. Viva White), tomato (*Lycopersicon esculentum*, var. Commune), and pepper (*Capsicum annum*) were sown in each compartment of the tray. The trays were then misted and placed in the greenhouse. No other cultural practices were changed except that the control had to be misted heavily to obtain wetting equivalent to the mixes treated with wetting agents. Germination and growth inhibition were observed 7 to 14 d later.

Previous work in our laboratories has shown that certain surfactants in solution and not adsorbed on soil surfaces can affect the membrane integrity of plant tissue. To determine inherent phytotoxicity, sheets of filter paper were placed in petri dishes, 7 ml of the appropriate concentration added, and 10 seeds of *Impatiens* (cv. Viva White) were sown on the moistened filter paper. The dishes were then covered, placed in the growth cabinet, and root length measured 14 d later.

Similarly, foliar tissue may also be affected by certain surfactants. In this test, *Impatiens* and pepper plants were grown to the five- to six-leaf stage and ryegrass to the 10-cm stage.

TABLE 1  
Comparative Foliar Toxicity of Three  
Surfactants

Rate (ml/300 m <sup>2</sup> )	<i>Impatiens</i>	Pepper	Ryegrass
AquaGro			
120	0 a	0 a	0 a
235	0 a	0 a	0 a
470	0 a	0 a	0 a
ACA-160			
120	0 a	0 a	0 a
235	0 a	0 a	0 a
470	1 a	0 a	0 a
ACA-196			
120	3 b	5 ab	4 ab
235	8 c	9 b	7 b
470	9 c	9 b	9 b
Control	0 a	0 a	0 a

Note: 0, no effect; 9, dead. Values are the means of three replicates. Means in a column followed by the same letter are not statistically different as determined by Duncan's multiple range test ( $p = 0.05$ ).

TABLE 2  
ACA-160 and AquaGro® Storage Study for  
Ease of Wetting in Open and Closed Bags

Storage time (weeks)	% Wet (200/200 percolation test)			
	ACA-160 (120 ml/m <sup>2</sup> )		AquaGro (350 ml/m <sup>2</sup> )	
	Open	Closed	Open	Closed
1	100	100	100	100
2	100	100	90	100
4	90	100	90	90
7	90	100	50	90
11	65	80	50	50
13	40	95	5	70
19	60	60	5	50
29	50	50	10	10

The plants were then sprayed to runoff with the equivalent rates shown in Table 1 to simulate field applications. Plant injury was observed 24 and 72 h later.

The ability of a mix to wet after drying is of concern to growers. To test ACA-160 under these conditions, mixes were prepared as previously described and a measured quantity placed in 950-ml (1.75-gal) zip-lock bags. One half of the bags were left open with the tops folded back to simulate a broken bale or pots filled, but not yet in use. The other half were closed to simulate a sealed bale. Two open and two closed bags were then sampled for ease of wetting at various storage times, as shown in Table 2. Samples from the open and closed bags were evaluated with a percolation test. In this test, 200 cc of peat or media were placed in a vertical tube with a screen on the bottom, and 200 ml of distilled water was added. The milliliters of water absorbed and the percent of wet media or peat were determined. Moisture loss was monitored throughout the course of the experiment in both open and closed bags.

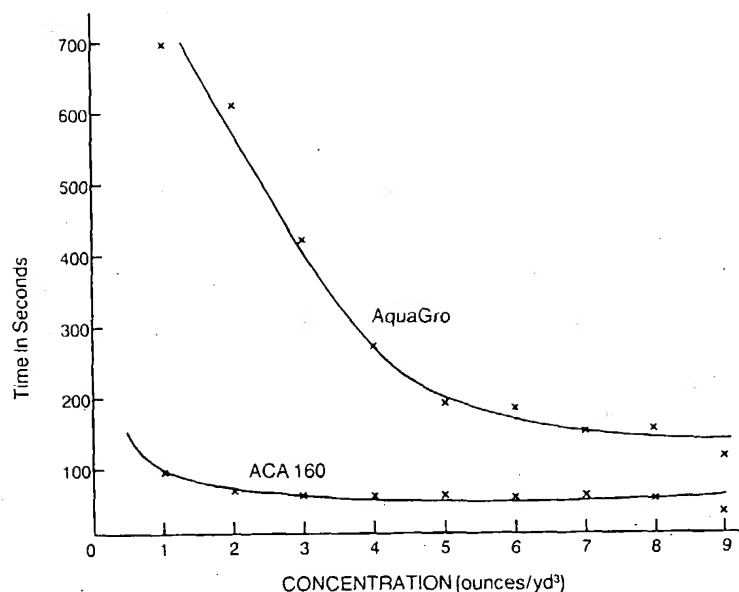


FIGURE 1. Wetting curves for two materials in a compacted peat medium. The value for the control (no wetting agent, not shown) is >900 s.

### III. RESULTS AND DISCUSSION

Ease of wetting of peat is dependent upon several factors, including the source of the peat, moisture content, degree of decomposition, and fiber length. The grower needs a medium which wets uniformly and absorbs and retains water. The peat used in the media is the primary vehicle for maintaining adequate moisture levels to support plant growth. Therefore, it becomes very important that the peat wets easily and quickly.

Results for speed and ease of wetting are shown in Figure 1. ACA-160 outperformed AquaGro® "L" at all rates tested. Of particular note is the fact that the inflection point (point at which the slope changes) of the wetting curve for ACA-160 was lower than 39 ml/m³, while that for AquaGro "L" was 175 ml/m³. These results show that ACA-160 is not only a faster wetter than AquaGro®, but is also effective at much lower concentrations.

Some plant species are very sensitive to certain surfactants, particularly during seed germination and early seedling growth. When used properly, existing products such as AquaGro "L" cause no detrimental effects. However, where errors may be made by either the grower or the mix manufacturer, the need for a greater safety margin exists. Results for germination and plant injury are shown in Table 3.

In Table 3, ACA-160 is compared with AquaGro "L". It should be noted that AquaGro® was used at recommended and greater than recommended rates for plug production.

Of the five species evaluated in this test, only *Impatiens* and *Begonia* responded, and then only at the 350-ml rate of AquaGro (recommended rate, 175 ml/m³ for plug production). No effect on germination or seedling morphology (including roots) was observed for ACA-160 at the concentrations tested. Depending upon the rate used, ACA-160 can be expected to have a three- to ninefold safety factor for wetting agent-sensitive species such as *Impatiens* or *Begonia* compared to AquaGro, which has a twofold safety margin.

Results of the determination of inherent phytotoxicity are shown in Table 4. Normally, the hydrophobe of the surfactant binds to the soil or peat particle; however, it is possible that a certain amount of the wetting agent might remain in the soil solution and affect plant

TABLE 3  
Comparative Effect on Plant Growth of Two Mix-  
Wetting Agents Used in Plug Production

Species	Control (no wetting agent)	Treatments (ml/m <sup>3</sup> )			
		ACA-160		AquaGro	
		120	350	120	350
Percent Germination					
<i>Impatiens</i>	85 a	85 a	85 a	85 a	45 b
Marigold	95 a	90 a	95 a	90 a	90 a
<i>Begonia</i>	80 a	85 a	85 a	80 a	40 b
Tomato	95 a	95 a	95 a	95 a	95 a
Pepper	90 a	95 a	90 a	95 a	90 a
Plant Injury					
<i>Impatiens</i>	0 a	0 a	0 a	0 a	6 b
Marigold	0 a	0 a	0 a	0 a	0 a
<i>Begonia</i>	0 a	0 a	1 a	0 a	7 b
Tomato	0 a	0 a	0 a	0 a	0 a
Pepper	1 a	0 a	0 a	0 a	0 a

Note: 0, no effect; 9, severely inhibited or dead. Values are the means of three replicates. Values in a row followed by the same letter are not statistically different as determined by Duncan's multiple range test ( $p = 0.05$ ).

TABLE 4  
Effect of Free Wetting Agent on  
Root Growth of *Impatiens* Grown  
on Moistened Filter Paper

Concentration (ppm)	Root length (cm)	
	AquaGro	ACA-160
1170	0 a	0 a
1000	0 a	5 a
833	0 a	5 a
667	5 a	10 ab
500	13 b	17 b
333	12 b	23 b
166	16 b	20 b
0 (Control)	20 b	19 b

Note: Values in a column followed by the same letter are not statistically different as determined by Duncan's multiple range test ( $p = 0.05$ ).

growth, particularly during reapplication. Consequently, materials are tested in solution to determine their effect. In this case, root length was less affected by free ACA-160 than by free AquaGro.

It is important that surfactants used for plant and soil applications do not harm plant foliage, as they may need to be applied over the foliage to the soil during production and for postharvest handling of the crop.

In this test, ACA-196 (a second experimental material), known to be toxic to plant tissue, was used as a standard of comparison. Neither AquaGro nor ACA-160 had a significant effect on foliage. ACA-196 as the positive control gave results typical of phytotoxic surfactants.

The preceding experiments point out important concepts which are often overlooked in dealing with surfactants and living plants. Depending upon chemistry, there may be dramatic differences in plant response, particularly in detrimental effects. Other researchers have also observed such differences.<sup>2,4,5</sup>

The last study of this report was designed to determine rewetting after storage of peat-lite mixes treated with ACA-160. The results are shown in Table 2.

Moisture loss was monitored throughout the course of the experiment in both open and closed bags. The open bags lost moisture quickly, but did not stabilize until week 11, after which little or no drying occurred. Closed bags also lost moisture, but at a much slower rate; however, by week 29, both open and closed bags had the same moisture content.

This gradual decrease in moisture content affected the performance of both products. Generally, rewettability is inversely proportional to the wetting agent and moisture content. This accounts for the gradual decline in the effectiveness of the two wetting agents with time. ACA-160 did, however, demonstrate its superior rewetting characteristics even after severe dehydration of the peat.

#### IV. CONCLUSIONS

It would appear that ACA-160 is superior to AquaGro®, the industry standard, in giving faster wetting, better wetting mixes with low moisture levels, and improved crop safety; it also can be used at lower rates than AquaGro (120 vs. 350 ml/m<sup>3</sup>).

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## Chapter 35

**A MECHANISTIC STUDY OF THE WETTING, SPREADING, AND  
SOLUTION PROPERTIES OF ORGANOSILICONE  
SURFACTANTS****E. D. Goddard and K. P. A. Padmanabhan****TABLE OF CONTENTS**

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## ABSTRACT

The special wetting, spreading, and solution properties of selected organosilicone surfactants have been investigated using such techniques as dynamic and static surface tension, wetting, spreading, adsorption, and turbidity measurement. It is shown that even fluorocarbon surfactants, which reduce the surface tension of water to values lower than that achievable by organosilicone surfactants, do not wet or spread on hydrophobic surfaces efficiently. The special wetting properties of organosilicone surfactants are attributed to their unique structure, ability to lower the liquid-air surface tension to low values, fast kinetics of adsorption at interfaces, high affinity of the surfactant for hydrophobic surfaces, and the favorable orientation and structure of the adsorbed molecules.

## I. INTRODUCTION

Wetting is an important industrial process which has engaged the attention of fundamental and applied investigators for over 100 years. Although it has long been appreciated, in a qualitative way, that low-energy surfaces such as wax, polyethylene, various leaves, etc. are more difficult to wet than high-energy surfaces, e.g., clean glass, metals, etc., it fell to Zisman<sup>12</sup> to systematize the phenomenon. He introduced the concept of a critical surface tension ( $\gamma_c$ ) for wetting a solid surface, according to which only liquids of surface tension ( $\gamma_l$ ) equal to or lower than  $\gamma_c$  would wet the surface completely. Finite contact angles ( $\theta$ ) would be observed for other liquids, with the size of the angle, in general, increasing with increasing surface tension. Despite the fact that interpretations of the theoretical significance of  $\gamma_c$  are still controversial and that there are restrictions concerning liquids to be chosen for the determinations, Zisman's concept has satisfactorily stood the test of time.

A tempting extension of the Zisman approach for determining  $\gamma_c$  is to use aqueous solutions of surfactants as the series of liquids of different surface tension. Serious difficulties with this approach arise from the fact that the surfactant molecules can adsorb on the solid surface and alter its wetting character; also, specific molecular effects in the surfactant can be observed. The latter effects, in fact, represent opportunities for the development of superior wetting systems, as may be illustrated in the following. Certain silicone surfactants, which can achieve very low surface tension values ( $\sim 20$  mN/m), have been shown to be able to wet the surface of polyethylene very effectively, whereas various fluorocarbon surfactants, well known for their ability to lower the surface tension of water to even lower values (16 mN/m or lower), are less efficient.

This chapter attempts to shed light on this subject, includes studies of the surface tension, wetting, and adsorption characteristics of a selection of three silicone surfactants, and presents a molecular mechanism to account for the unusually efficient wetting ability of one of them.

## II. MATERIALS AND METHODS

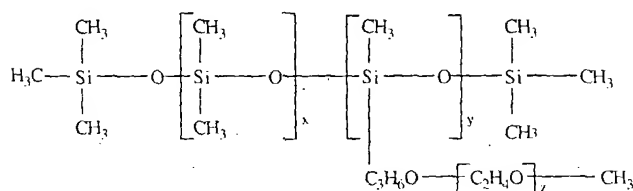
### A. MATERIALS

The three nonionic silicone surfactants used in this work are designated SS-1, SS-2, and SS-3. See Table 1 for their structure and other properties. They were synthesized by the procedures of Bailey and Snyder.<sup>3</sup> Tergitol® NP-10, a nonylphenol 10-mol (average) ethoxylate, is a product of Union Carbide Corporation. A series of fluorocarbon surfactants, FSA (anionic), FSB (zwitterionic), and FSN (nonionic), was obtained from DuPont. The sodium dodecyl sulfate was a high-purity specimen from EM Sciences. Polyethylene powder (Polymist® B-6, average particle size 6  $\mu$ m) was obtained from Allied Signal.

TABLE I  
Properties of Surfactants

Property structure <sup>a</sup>	SS-1	SS-2	SS-3
	(x = 0, y = 1, z = 7.5)	(x = 0, y = 1.5, z = 7.5)	(x = 20, y = 3.2, z = 7.5)
Molecular weight	620	855	3120
% EO	53	58	3
Cloud point	0—20°C	43—53°C	0—20°C
Surface tension, bulk mN/m	24.1	25.2	21.6
Surface tension, 1% solution	20.7	22.4	22.1

<sup>a</sup> Nominal formula and structure:



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## B. METHODS

Surface tension was measured by the Wilhelmy plate technique using a Cahn electrobalance and a sandblasted platinum plate as sensor. Wetting of polyethylene film or Parafilm® (paraffin wax film) was carried out as follows. A 50- $\mu\text{l}$  drop of surfactant solution (0.1%) was carefully placed on the horizontal film, and after 5 min, the diameter of the spread drop was measured. The "spreading factor" refers to the diameter of the drop of a solution divided by that achieved by a drop of water. Wetting experiments, under quiescent conditions, were done by carefully placing a fixed amount (0.1 g) of polyethylene powder on the surface of the solution and measuring the time for complete wetting. An instantaneous increase in surface tension occurred on placement of the powder because of the extraction of surface-adsorbed surfactant. This change of surface tension would, of course, depend upon the rate of extraction of surfactant from the interface and subsurface region. The surface tension changed slowly after the initial increase and finally attained a new equilibrium value which corresponded to complete wetting, thereby affording a means to monitor wetting time.

Adsorption measurements were carried out by contacting a fixed weight (1 g) of polyethylene powder with a 20-ml volume of the various surfactant solutions contained in vials. Agitation was carried out for 1 h in a wrist-action shaker. Thereafter, the solution was separated from the solid by centrifugation and analyzed by total carbon analysis with a Beckman Tocamaster. Turbidity of selected solutions was measured by means of a Hach turbidimeter (Model 2100).

## III. RESULTS AND DISCUSSION

The surface tension data, represented in the form of  $\gamma$ -log C plots, are presented in Figure 1. Both effectiveness and efficiency of surface tension lowering are in the order SS-1 > SS-2 > SS-3. Noteworthy is the low surface tension value of 20 mN/m attained by

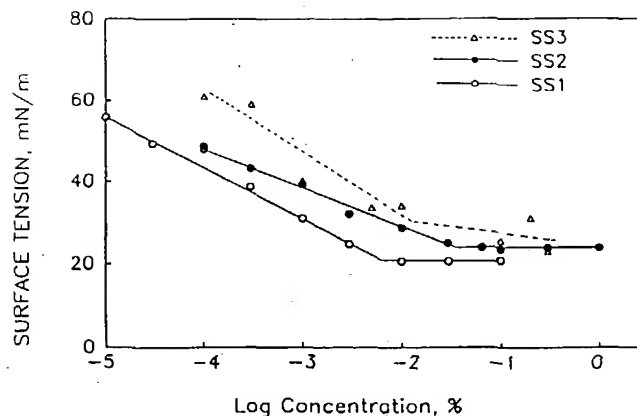


FIGURE 1. Surface tension vs. log concentration plots for aqueous solutions of silicone surfactants SS-1, SS-2, and SS-3. (From Ananthapadmanabhan, K. P. et al., *Colloids and Surfaces*, Elsevier-Science Pub., Amsterdam, 44, 281, 1990. With permission.)

SS-1 solutions, which is equal to the surface tension of liquid silicones and can be viewed as the ultimate value achievable by a silicone surfactant in aqueous solution.<sup>10</sup>

It is reasonable to assume that at the air-water interface, silicone surfactants will orient in the classical way, i.e., have their hydrophilic group immersed in water and their hydrophobic group in air. Paradoxically, however, the structure of SS-1, with its compact hydrophobic group and extended hydrophilic polyether chain, seems like an "inversion" of the structure of a regular ionic surfactant, possessing a compact polar head group and a long hydrophobic alkyl chain (Figure 2A). It would not be surprising if this "inversion" endowed the SS-1 molecule with special, if not unique, properties. Particularly noteworthy is the high density of the hydrophobic methyl groups allowed by the short silicone backbone and evident in the "plan" view of the SS-1 molecule in Figure 2B. Hartley<sup>8</sup> has pointed out the effectiveness in a surfactant molecule of a compact hydrophobic group and a long hydrophilic group. Moreover, Adam and Elliott<sup>1</sup> demonstrated that a "CH<sub>3</sub>" surface is more hydrophobic than a "CH<sub>2</sub>" surface. These considerations can explain the high level of effectiveness of silicone surfactants, especially that of SS-1.

The area per molecule deduced from the limiting slope of the  $\gamma$ -log C plot, and the Gibbs equation, is 70 Å<sup>2</sup>/mol for SS-1 and 90 Å<sup>2</sup>/mol for SS-2, presumably corresponding to near close-packing of the silicone hydrophobic groups.

SS-1 and SS-2 exhibit sharp breaks in their  $\gamma$ -log C plots, suggesting the existence of a critical concentration and the formation of micelles. However, the development of turbidity — in the case of SS-1, at a concentration close to the break point (~0.02%) — shows that this conclusion is premature. SS-2 solutions, on the other hand, are clear up to the 5% level, the highest concentration tested. SS-3 solutions, which do not show a sharp break point, appear to be turbid, yet physically stable, over all concentrations tested. An attempt was made to determine the size of SS-2 micelles by photon correlation spectroscopy, but the micelles were undetectable in our instrument, implying a size of less than 100 Å.

Additional work, reported elsewhere,<sup>2</sup> was undertaken to further characterize the nature of the dispersed species in aqueous solutions of the three surfactants. The results obtained by the fluorescence probe method, can be summarized as follows. With pyrene as the probe, the fluorescence characteristics showed that as the concentration of SS-1 and SS-2 is raised through the "critical concentration" region, the pyrene experienced a change from a hydrophilic to a more hydrophobic environment, with the change being sharper in the case of SS-1. Carrying out so-called dynamic fluorescence measurements with a higher pyrene

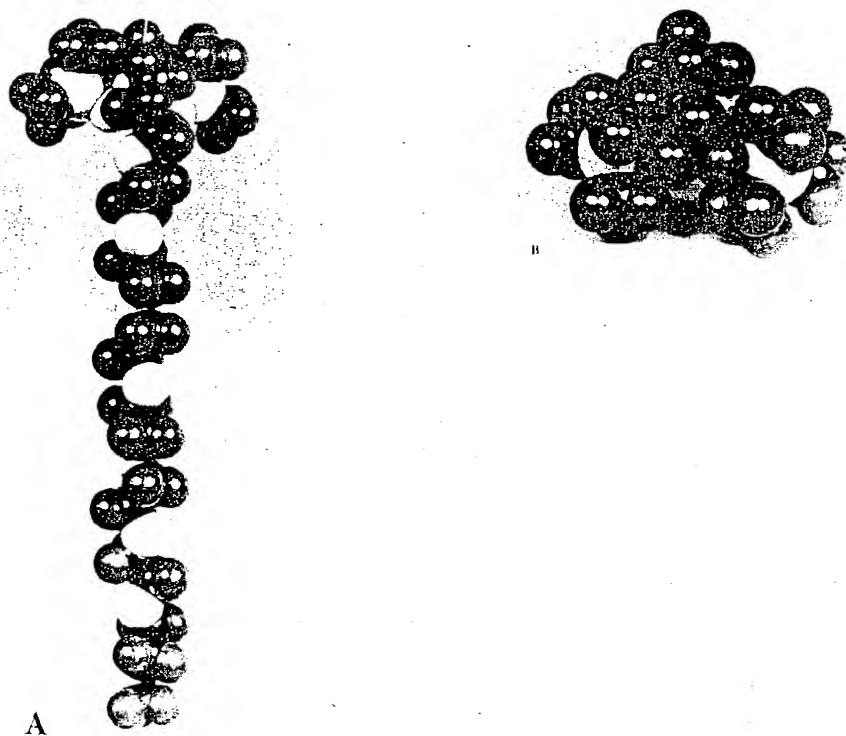


FIGURE 2. (A) A space-filling model of silicone surfactant SS-1; (B) "plan view" of SS-1 molecule. Both photographs illustrate the compact nature of the hydrophobic "head" group. (From Ananthapadmanabhan, K. P. et al., *Colloids and Surfaces*, Elsevier-Science Pub., Amsterdam, 44, 281, 1990. With permission.)

concentration ( $\approx$  the molar concentration of micelles) and observing the decay of fluorescence allowed calculation of the aggregation number ( $N$ ) of the SS-2 micelle, which turned out to be 31 monomers.

#### A. WETTING OF POLYETHYLENE

We have referred already to the superior wetting ability of various silicone surfactants. Representative spreading factor data for the wetting of Parafilm are given in Table 2. It is seen that fluorocarbon surfactants, which generate aqueous surface tensions as low as 16 mN/m, do not wet the surface as efficiently as SS-1 and SS-2. Evidently, surface tension is not the only criterion governing the wetting of this low-energy surface.<sup>4-6,9</sup>

Wetting tests of polyethylene powder gave further insight and allowed further discrimination among the surfactants. On placement of the powder upon the surface of SS-1 solutions of concentration  $>0.005\%$ , wetting was observed to begin at the periphery of the powder aggregate and, as the process progressed, the wetted particles became dislodged from the mass in a very vigorous way. Somewhat similar behavior, but with less vigorous wetting, occurred with SS-2 at concentrations  $>0.03\%$ . In contrast, SS-3 did not exhibit the rapid wetting behavior, nor did conventional nonionic surfactants or fluorocarbon surfactant FSB at 0.1 or 1% concentrations wet the polyethylene powder.

Although kinetic effects are clearly involved in the preceding phenomena, it is appropriate to examine the thermodynamic criteria for spreading and wetting/immersion. Spreading



TABLE 2  
Spreading Ability of Various Surfactants Relative to  
Water

System	Spreading factor	Surface tension
Water	1.0	72.8
SS-1	8.6	20.5
SS-2	2.3	23.5
Fluorocarbon surfactant, FSA <sup>a</sup>	2.0	16.2
Fluorocarbon surfactant, FSB <sup>a</sup>	1.8	16.8
Nonionic surfactant Tergitol NP-10 <sup>b</sup>	1.7	31.1
Fluorocarbon surfactant, FSN <sup>a</sup>	1.4	23.4
Sodium dodecyl sulfate	1.2	44.3

Note: Surfactant concentration, 0.1%.

<sup>a</sup> Obtained from E. I. duPont de Nemours & Company, Inc., Wilmington, DE 19898.

<sup>b</sup> Obtained from Union Carbide Corporation, New York, NY.

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involves the replacement of the solid-gas (SG) interface by solid-liquid (SL) and liquid-gas (LG) interfaces, and will occur if the free energy ( $\Delta G_s$ ) of the process

$$\Delta G_s = \gamma_{SL} + \gamma_{LG} - \gamma_{SG}$$

is negative. This is tantamount to the spreading coefficient,  $S$ , which equals  $-\Delta G_s$ , being positive.

Immersion of the solid powder involves replacement of the SG interface by the SL interface. Hence, immersion is favored if the free energy ( $\Delta G_i$ ) of immersion

$$\Delta G_i = \gamma_{SL} - \gamma_{SG}$$

is negative. Note that if  $\Delta G_s$  is negative, then  $\Delta G_i$  must be negative, i.e., if the conditions for spreading are favorable, then, energetically, those for wetting/immersion must be favorable.

We have mentioned that dynamic effects, as well as formal surface energies, play a role in wetting/spreading. Involved are molecular events, including adsorption, subsurface layer depletion, and surface and bulk diffusion.

First, however, we present data which seem to confirm the effectiveness of a low surface tension. SS-1 at the 0.005% level ( $\gamma = 21.5$  mN/m) wets the powder in about 8 min, whereas SS-2 at the higher solution concentration of 0.003% ( $\gamma = 24$  mN/m) requires 40 min. We point out again that  $\gamma_c$  for polyethylene is 31 mN/m.

The influence of adsorption kinetic effects can be inferred from the following: considering three solutions of about the same surface tension, we see that 0.1% SS-2 solution wets polyethylene powder in 2.7 min, much faster than both 0.03% SS-2 (40 min) and 0.003% SS-1 (60 min), presumably as a result of faster diffusion/adsorption at the expanding liquid-solid interface at the highest surfactant concentration (Table 3). On the other hand, a 0.01% SS-1 solution ( $\gamma = 21.5$  mN/m) gives complete wetting in 1.2 min, whereas SS-2 at ten times the concentration ( $\gamma = 23.5$  mN/m) wets, at best, in a comparable (actually somewhat

TABLE 3  
Wetting Times

Conc (%)	SS-1		SS-2	
	mN/m	Wetting time (min)	mN/m	Wetting time (min)
0.003	23.5	60	—	—
0.005	21.5	8	—	—
0.01	21.5	1.2	—	—
0.03	—	—	24	40
0.1	—	—	23.5	2.7

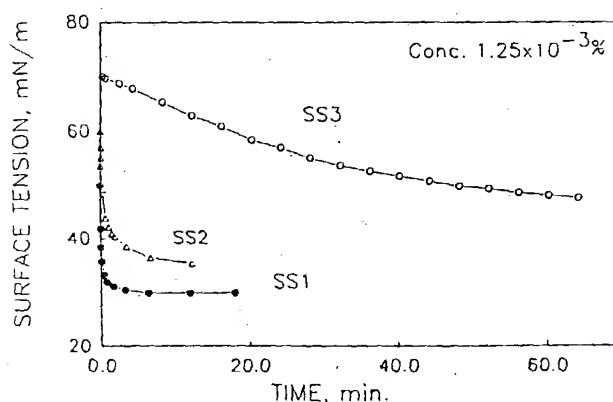


FIGURE 3. Dynamic surface tension of aqueous solutions of silicone surfactants SS-1, SS-2, and SS-3. (From Ananthapadmanabhan, K. P. et al., *Colloids and Surfaces*, Elsevier-Science Pub., Amsterdam, 44, 281, 1990. With permission.)

longer) period of time, showing again the favorable influence of low surface tension and probably also that specific molecular effects can offset the favorable kinetic influence of higher concentration. The higher mobility of SS-1 molecules *vis a vis* SS-2 molecules is evident from kinetic results for their adsorption at the air-water and solid-water interfaces (Figure 3, Table 4). The dynamic surface tension lowering is faster for SS-1 than for SS-2, allowing the conclusion that any SS-1 molecules "lost" from the air-water interface will be rapidly replenished by adsorption. Although in generating the adsorption data in Table 4 for SS-1 and SS-2 at the solid (polyethylene powder)-water interface, agitation conditions were used (unlike the film-wetting studies), differences in adsorption rates of the two surfactants can again be seen.

It is interesting that rapid wetting is not restricted to polyethylene. Rapid wetting of hydrophobic silica also occurs in SS-1 solutions, but starting at higher concentrations, viz., 0.01%, in this case. We note that the  $\gamma_c$  for wetting a "CH<sub>3</sub>"-covered surface (23 mN/m) is appreciably lower than the  $\gamma_c$  for polyethylene (31 mN/m).

Further data on the adsorption of SS-1 and SS-2 on polyethylene powder are given in Tables 5 and 6, which present equilibrium results. The presence of a "plateau" signifies monolayer adsorption, and in this region, the saturation adsorption values of SS-1 and SS-2 are comparable. In the low concentration range, however, more SS-1 than SS-2 is adsorbed. These results are consistent with the surface-wetting results inasmuch as complete wetting with SS-2 occurs at a much higher concentration than for SS-1.

TABLE 4  
Kinetics of Adsorption of  
SS-1 and SS-2 on  
Polyethylene Powder  
(Solution Agitated)

Time (min)	Adsorption (mol/g)	
	SS-1	SS-2
0	0	0
1	$1.3 \times 10^{-6}$	0
3	$2.9 \times 10^{-6}$	$1.7 \times 10^{-6}$
10	$2.9 \times 10^{-6}$	—
15	—	$2.0 \times 10^{-6}$
20	$2.9 \times 10^{-6}$	$2.0 \times 10^{-6}$

Note: Initial surfactant concentration  
0.02%.

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mission.

TABLE 5  
Adsorption of SS-1 on  
Polyethylene Powder  
(Solution Agitated)

Initial conc (%)	Adsorption (mol/g)
0.003	$6.65 \times 10^{-7}$
0.01	$2.14 \times 10^{-6}$
0.02	$3.07 \times 10^{-6}$
0.03	$3.44 \times 10^{-6}$
0.1	$3.44 \times 10^{-6}$
0.3	$3.68 \times 10^{-6}$

Note: System polyethylene powder  
(6-  $\mu$ m size); 1 g solid, 20 g  
solution.

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From the plateau adsorption values, and on assuming a surface area of  $1.1 \text{ m}^2/\text{g}$  for polyethylene powder (average particle size,  $6 \mu\text{m}$  density,  $0.93 \text{ g/cm}^3$ ), the area per molecule of both SS-1 and SS-2 is calculated to be about  $50 \text{ \AA}^2/\text{molecule}$ , a reasonable value for the packing area of the SS-1 hydrophobic head group. This indicates that the adsorbed layer is more compact at the solid-liquid interface than at the liquid-air interface.

TABLE 6  
Adsorption of SS-2 on  
Polyethylene Powder  
(Solution Agitated)

Initial conc (%)	Adsorption (mol/g)
0.005	$5.4 \times 10^{-7}$
0.01	$1.3 \times 10^{-6}$
0.03	$2.5 \times 10^{-6}$
0.1	$2.9 \times 10^{-6}$
1.0	$3.8 \times 10^{-6}$

Note: System, polyethylene powder  
(6- $\mu$ m size); 1 g solid, 20 g  
solution.

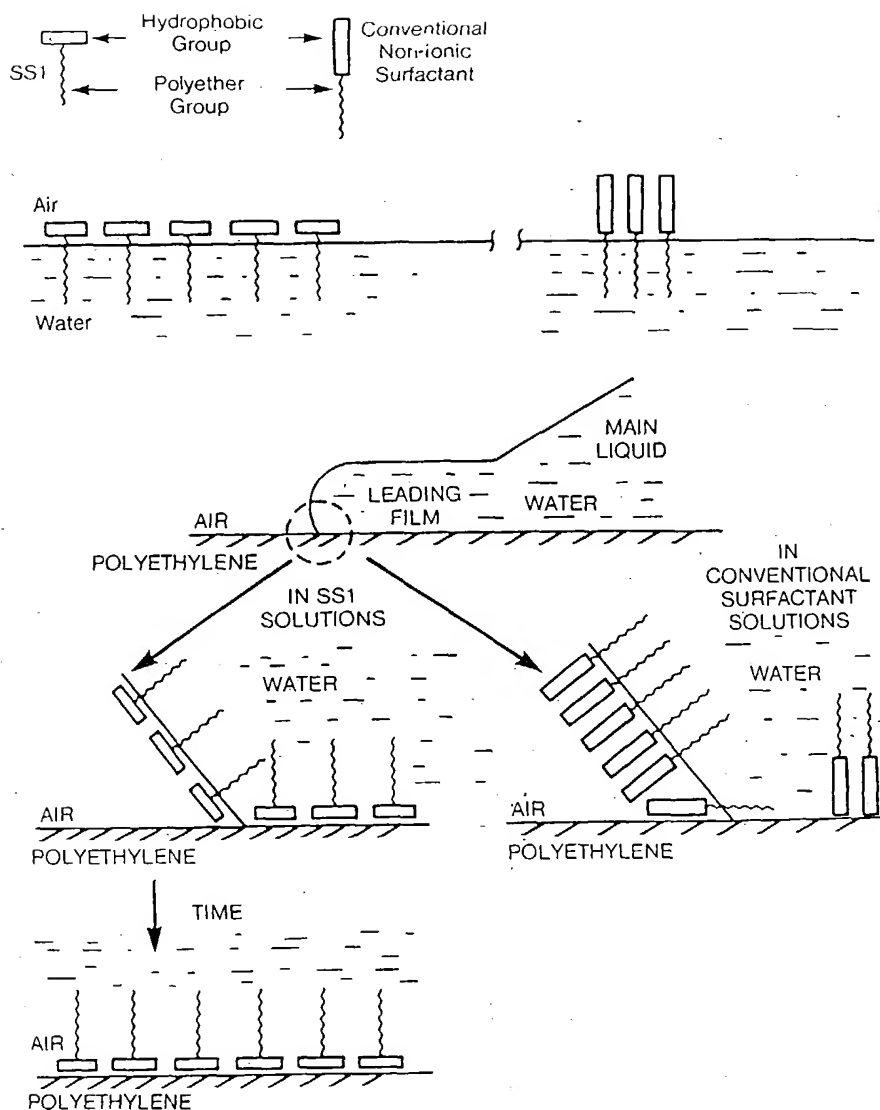
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## B. SPREADING PROCESS

Hardy,<sup>7</sup> in his classical study of the spreading of polar liquids on glass and steel, postulated that the leading edge of the spreading fluid is actually a thin, virtually invisible satellite film of liquid about 1  $\mu$ m thick; furthermore, that the surface tension of this primary film is higher than that of the bulk of the spreading fluid and, in consequence, the latter is pulled forward. This picture is very realistic for a solution of a surfactant where, because of adsorption at the solid-liquid interface, the surface tension of the primary film would be increased. The fast kinetics of adsorption of SS-1 molecules at the solid-liquid and liquid-gas interfaces would help to replenish the leading edge quickly with surfactant molecules. We believe, moreover, that the unique ability of SS-1 molecules to spread on hydrophobic surfaces is related to their compact structure, which facilitates a transfer of surfactant molecules from the liquid-air interface to the solid surface. A depiction of possible events at the liquid interface during spreading is presented in Figure 4. Note that the dynamic advancing angle of the satellite film is shown, on a molecular scale, as being obtuse — a real possibility in our view. Because of their compact nature, efficient adsorption, and packing, SS-1 molecules are readily transferred to the polyethylene surface, facilitating the progressive advance of the liquid film in a process which can be likened to "molecular zippering" of the polyethylene-water interface. This behavior can be contrasted to that observed with conventional (and other silicone) surfactants in which the more cumbersome hydrophobic groups impede the molecular transfer and wetting process. On this basis, it is understandable why "contaminant" surfactant molecules (adventitious or deliberately added) can interfere with the molecular processes involved in the wetting action of SS-1.

Direct determination of the thickness of the adsorbed surfactant layer and that of the leading edge of the spreading film, together with the advancing contact angle, would provide considerable insight into the spreading process. Attempts to do this are underway in our laboratory.

We mention, in closing, that the efficiency of wetting of plant leaves by solutions of silicone surfactants has frequently been reported; see, for example, Reference 11.



**FIGURE 4.** A schematic depiction of transfer of surfactant molecules from the liquid-air interface to the polyethylene surface. The progressive advance of SS-1 solutions can be likened to "molecular zippering" of the polyethylene-water interface. Conventional surfactants tend to lie flat on the surface, exposing hydrophobic patches which impede spreading. (From Ananthapadmanabhan, K. P. et al., *Colloids and Surfaces*, Elsevier-Science Pub., Amsterdam, 44, 281, 1990. With permission.)

#### IV. CONCLUSIONS

Silicone surfactants represent a group of surface agents in which an array of methyl groups bonded to silicone atoms constitute the hydrophobic part of the molecule, as opposed to methylene groups (albeit with a single terminal methyl group) in conventional surfactants. This structure evidently endows the silicone surfactants with special surface activity, since they are able to lower the surface tension of water to as low a value as 20 mN/m and also



to wet hydrophobic surfaces very efficiently. The special wetting ability of one of the silicone surfactants (SS-1) is associated with its rapid adsorption at the air-water interface and efficient transfer to the surface of the solid in view of its unique compact structure.

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## Chapter 36

**PATHWAYS AND MECHANISMS OF FOLIAR UPTAKE AS  
INFLUENCED BY SURFACTANTS**

Peter J. G. Stevens, Robyn E. Gaskin, Sung-Ok Hong, and Jerzy A. Zabkiewicz

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## ABSTRACT

Deoxyglucose (DOG), a model active ingredient (a.i.), and glyphosate have been used to investigate the effects of surfactants on the kinetics of the foliar uptake process using radiochemical methods. The organosilicone surfactant Silwet® L-77 (0.5%) enabled spray solutions to infiltrate the stomatal pores, providing levels of uptake of 50% into bean, 35% into oat, and 20% into winter wheat within 10 min of application. Silwet L-77 apparently did not enhance subsequent cuticular penetration, but various other surfactants, both organosilicones and "conventionals" (nonorganosilicones), did. The mechanism of nonstomatal enhancement of uptake was more commonly an increased proportion of a.i. ultimately absorbed rather than an increase in the rate of cuticular penetration. The effects of surfactants on uptake were species specific.

## I. INTRODUCTION

The cuticle covering the aerial surfaces of all plants<sup>12</sup> presents a barrier to the entry into the tissues of foliar-applied agrichemicals.<sup>11,18</sup> Stomata provide a direct route of access to the leaf interior. Advantages likely to result from the infiltration of stomatal pores by spray solution are:

1. The a.i. taken up in this manner is immediately rendered rainfast.
2. Other factors which also may erode deposits of a.i. on the exterior of foliage, e.g., volatilization and photodegradation, are attenuated.
3. Penetration of a.i. into the tissues is facilitated by the relatively thin cuticle lining and large surface area of the convoluted intracellular air spaces.
4. Deposition of a.i. within the leaf in close proximity to the vascular tissues may assist translocation and thus enhance systemic activity.

Stomata have been implicated in the foliar uptake process on numerous occasions and, in general, it has been concluded that stomata are sites of preferential cuticular penetration.<sup>4,20</sup> However, claims have been made that stomata are portals for the entry, by mass flow, of spray solutions into leaves.<sup>19</sup> The physical requirements for solutions to infiltrate stomata have been investigated.<sup>22</sup> It is clear that the surface tensions (about 30 mN m<sup>-1</sup>) typically provided by the surfactants in agrichemical sprays will enable only a small proportion of stomata, if any, to be infiltrated.<sup>7</sup> However, organosilicone surfactants can reduce aqueous surface tensions to 20 to 25 mN m<sup>-1</sup>. One of these, Silwet L-77, has long been known to have the ability to induce stomatal infiltration,<sup>16</sup> an effect which is readily visualized.<sup>30</sup> However, the contribution of stomatal infiltration to enhancements of foliar uptake by Silwet L-77 has not been determined satisfactorily.<sup>3</sup>

Stomatal infiltration can occur only in the brief period after application, while spray deposits remain liquid. Thereafter, cuticular penetration remains as the sole pathway of uptake. Although reports of enhancements of foliar uptake by surfactants are manifold, only rarely has evidence been produced to support specific mechanisms for these enhancements. One such mechanism is the copenetration of surfactant and a.i.,<sup>26</sup> which appears to affect the rate of penetration.<sup>23</sup> The kinetics of foliar uptake have rarely been investigated in detail.<sup>1,13</sup> The rate of uptake has generally been found to decline exponentially with increasing time after application, as anticipated for a process which is assumed to be a pseudo first-order reaction.<sup>9</sup> Certain studies have also demonstrated that, even after an extended interval, a large proportion of chemical may remain unabsorbed, but that this proportion is affected by formulation.<sup>14</sup>

The present study was designed to investigate the time course of foliar uptake as affected by the addition of Silwet L-77 in comparison with four other surfactants. The objectives were (1) to ascertain the relative contributions of the stomatal and cuticular pathways of uptake and (2) to determine if the mechanism of enhanced cuticular penetration was related to an increased rate of penetration and/or an increased proportion of a.i. ultimately taken up.

## II. MATERIALS AND METHODS

### A. SURFACTANTS

The surfactants used were Silwets L-77, L-7607, and Y-12301 (Union Carbide, NY), the latter an experimental Silwet product, all polyalkylene oxide-modified dimethylpolysiloxanes. In addition, a mixture of Silwets L-77 and L-7607 (1 + 1 by weight) was included. Two "conventional" surfactants were also used: Agral® 90 (nonylphenoxypolyethoxyethanol, mean EO 9, plus 10% propan-2-ol, ICI, U.K.) and Triton® X-45 (octylphenoxypolyethoxyethanol, mean EO 4.5, Rohm & Haas, PA).

### B. CHEMICALS

2-Deoxy-D-[U-<sup>14</sup>C]glucose (Amersham, 99% pure) was diluted as necessary with unlabeled chemical (Aldrich, 99% pure) and dissolved at 7.2 g l<sup>-1</sup> in water. *N*-(phosphono[<sup>14</sup>C]methylglycine) (glyphosate, Amersham, 98.4% pure) with an equimolar quantity of 2-aminopropane (Aldrich, 99% pure) was diluted with either unlabeled glyphosate monoisopropylamine (Monsanto, analytical grade) or Roundup® to provide aqueous solutions of 7.2 g of acid equivalent (a.e.) per l (equivalent to 1 l of Roundup in 50 l of water).

### C. PLANTS

Bean (*Vicia faba* cv. Evergreen), oat (*Avena sativa* cv. Amuri), and winter wheat (*Triticum aestivum* cv. Advantage) were grown from seed in pots (70 mm) containing granulated bark incorporating magnesium ammonium phosphate (2 kg m<sup>-3</sup>). The plants were illuminated with 500 to 550 μmol m<sup>-2</sup> s<sup>-1</sup> (400 to 700 nm) for 11.5 h daily by mercury vapor lamps with a 1% red light supplement provided by tungsten lamps. The red light extended for 0.5 h on either side of the main photoperiod to provide dawn and dusk periods during which the temperature was ramped smoothly between the night (15°C) and day (20°C) temperatures. Relative humidity (RH) was maintained at a constant 70%, and water was supplied once daily as required. Response Black Label® 9-4-6 (Growth Marketing), an NPK-enriched liquidized seaweed fertilizer, was applied (2 ml l<sup>-1</sup>) weekly. The stomatal status of bean plants was determined by measuring the diffusive resistance of leaves using an LI-1600 porometer (Li-Cor).

### D. FOLIAR UPTAKE

Droplets (0.24 μl, equivalent to 770 μm inflight diameter) were applied by microsyringe to the adaxial surface of fully expanded leaves on individual plants: bean, 20 drops on a single leaflet of the third or fourth leaf (fifth or sixth leaf emerging, respectively); oat and wheat, 10 drops on the second leaf (third leaf expanding fourth leaf emerging). Applications to bean (leaf area 15.3 ± 0.9 cm<sup>2</sup>; leaf area index 1.6 ± 0.3; 100 plants, m<sup>-2</sup>) were equivalent to 50 l ha<sup>-1</sup>. Applications were made in the dark 2.25 to 1.25 h before the start of the main photoperiod, and in the light 0.75 to 1.75 h after commencement of the main photoperiod. For applications in the "dark", sufficient light for work purposes (<1 μmol m<sup>-2</sup> s<sup>-1</sup>) was supplied by orange-tinted tungsten lamps, and the temperature was ramped

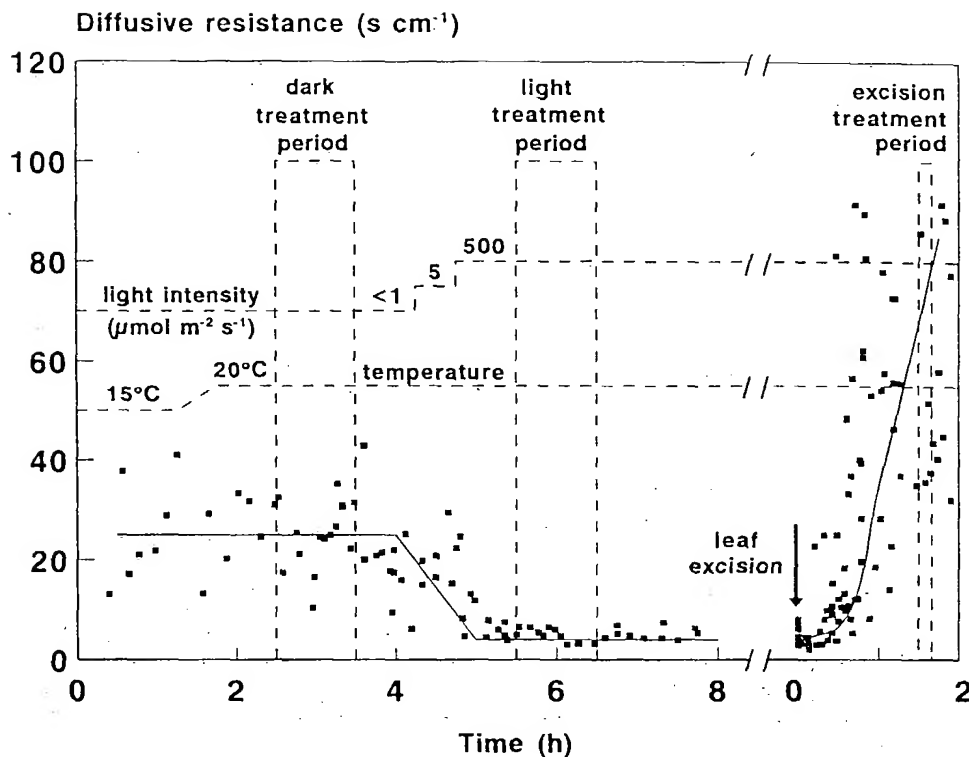


FIGURE 1. Stomatal status of bean leaves at time of treatment in relation to illumination and temperature.

up to "light" level (20°C) in the period 1.25 to 0.75 h prior to the start of applications (Figure 1). Applications in the light were duplicated on leaves which had been excised 1.5 h previously. The quantity of  $^{14}\text{C}$ -chemical applied to leaves was determined by dispensing droplets (five) directly into scintillation vials (minimum of five replicates). Leaves (minimum of five replicates) were sampled at a minimum of five time intervals between 10 min and 6 h postapplication for attached leaves, but only after 10 min for excised leaves. In certain cases, additional samples were taken as late as 45 h postapplication. The interval between sampling times was increased roughly exponentially, such that the increase in uptake between sets of samples was fairly uniform throughout the time course. When sampled, the attached leaves were excised and the treated (adaxial) surface washed with  $2 \times 4$  ml of water + ethanol (1 + 1 by volume) to recover unabsorbed  $^{14}\text{C}$ -chemical. The recovery provided by this wash immediately after droplet drying was  $\geq 96\%$  for chemicals applied without surfactant. The washings were taken up in 10 ml of ACS II scintillant (Amersham) and the  $^{14}\text{C}$  quantified by liquid scintillation counting. When DOG was applied to bean, the leaves sampled 6 h postapplication were oxidized (Harvey) to determine translocation. Preliminary experiments had demonstrated that all the  $^{14}\text{C}$  applied could be recovered when all plant tissues, including roots, were sampled.

#### E. ANALYSIS OF DATA

Foliar uptake was defined as  $^{14}\text{C}$  not recovered by washing the treated leaf and was calculated as a percentage of that applied. Likewise, translocation was expressed as a percentage of applied  $^{14}\text{C}$ , being defined as  $^{14}\text{C}$  not recovered in either the wash or from the treated leaf. The Genstat 5 computer program (Lawes Agricultural Trust) was utilized



TABLE 1  
Effect of Surfactant (0.5%), Illumination, and Leaf  
Excision (1.5-h Preapplication) on Uptake of  
Deoxyglucose into Bean Leaf During Initial 10-Min  
Postapplication

Treatment	Percent uptake		
	Attached leaves		Excised leaves
	Light	Dark	Light
Control (no surfactant)	4.5 d	6.4 cd	10 bc
Agral 90	4.4 d	4.7 d	12 b
Triton X-45	7.5 c	6.0 cd	7.7 c
Silwet L-7607	8.8 c	7.4 c	9.1 bc
Silwet Y-12301	29 a	11 bc	11 bc
Silwet mixture	36 a	17 b	ND
Silwet L-77	49 a	44 a	11 bc

Note: Treatments with letters in common are not significantly different at  $p = 0.05$ . ND, not determined.

for statistical analysis of results. Exponential models of the time courses of uptake were fitted to data: % uptake =  $A - (B \times S^T)$ , where  $A$  = asymptote,  $A - B$  = intercept,  $S$  = slope factor (i.e., rate of uptake), and  $T$  = time of postapplication in hours. Comparisons among treatments were made using F-tests for each parameter of the model and by examination of confidence intervals for the data of treatments which did not fit an exponential model.

### III. RESULTS AND DISCUSSION

#### A. STOMATAL INFILTRATION

Cuticular penetration also occurs during the period immediately after application, when stomatal infiltration is possible. Indeed, the rate of penetration from solution is markedly greater than that from dry spray deposits.<sup>28</sup> Nonetheless, it is apparent that the contribution of penetration to overall foliar uptake during this period will be minor, relative to that provided by a mass flow of solution through the stomatal pores. Thus, high levels of uptake within a few minutes of application are indicative of stomatal infiltration. Infiltration is proven if conditions which induce stomatal closure also reduce uptake.

Addition of Agral 90 had no effect on the initial uptake of DOG into attached leaves of bean in the light (Table 1). Both Triton X-45 and Silwet L-7607 significantly increased uptake, but by less than twofold. This increase must be considered with regard to the relative wetting abilities of these surfactants. Triton X-45 and Silwet L-7607 are better wetters than Agral 90,<sup>32</sup> and thus provided larger interfacial areas, enabling greater penetration of DOG into the leaf. The Silwet mixture and Silwets L-77 and Y-12301 markedly enhanced, by six- to 11-fold, the initial uptake of DOG. Although these surfactants are even better wetters than Triton X-45 and Silwet L-7607, it is implausible that the uptake of up to 50% of DOG, a highly polar compound, within 10 min of application could be attributable to cuticular penetration. It was notable that uptake, in the presence of Silwet Y-12301 and the Silwet mixture, was reduced more than twofold when DOG was applied in the dark, when the stomata were expected to be closed. However, uptake in the presence of Silwet L-77 was not significantly reduced. This apparent anomaly was explained by porometric measurements which demonstrated that while the stomata were definitely open in the light, they were only

TABLE 2  
Effect of Surfactant (0.5%) and Illumination on Time Course (10-min to 6-h Postapplication) of Uptake of Deoxyglucose into Bean Leaf

Surfactant	Light/dark	% Uptake = $A - (B \times S^{\text{Time in h}})$			Coefficient of determination (R <sup>2</sup> as %)
		Asymptote (A)	Intercept (A - B)	Slope (S)	
Control (no surfactant)	L	21 ag	2.1 f	0.57 a	70
Agral 90	L	25 bg	3.1 f	0.78 a	75
Triton X-45	L	33 bh	4.2 f	0.74 a	82
Silwet L-7607	L	45 d	6.1 f	0.85 a	62
Silwet mixture	D	40 cd	7.1 f	0.26 b	38
Silwet L-77	L		38* bd	NS	
	D		40* cd	NS	
	L		51* e	NS	
Silwet Y-12301	D		20* a	NS	
	L		31* b	NS	

Note: Within columns, treatments with letters in common are not significantly different at  $p = 0.05$ ; asymptotes may be compared with intercepts. NS, not significant (i.e., no significant increase in uptake with time).

\* Mean uptake for all samples, regardless of time.

partially closed in the dark (Figure 1). Therefore, leaves were excised to induce definitive stomatal closure.<sup>15</sup> The mean diffusive resistance of leaves 1.5 h after excision was about three times that of attached leaves in the dark (Figure 1).

Uptake into excised leaves from solutions incorporating Silwets L-77 and Y-12301 was reduced to levels not significantly different from those in the presence of Triton X-45 and Silwet L-7607 (Table 1). The latter two treatments were not affected by leaf excision. This confirmed that the high levels of initial uptake produced by addition of the Silwet mixture and Silwets L-77 and Y-12301 were attributable to the infiltration of stomata. For each of these three treatments, increased transmission of light by the leaf tissues had been observed in the vicinity of many of the droplets applied as a result of waterlogging of the intercellular air spaces. Obviously, excised leaves are not a physiologically representative system. However, the infiltration of stomata by solutions is a purely physical process and there is no evidence for the direct involvement of biological factors. Thus, the significant increase of uptake into excised, relative to attached, leaves in both the absence of surfactant and presence of Agral 90 remains unexplained. The apparent absence of any effect of leaf water potential on the contact angle of aqueous droplets on the leaf surface<sup>31</sup> negates altered wetting as an explanation for this phenomenon.

## B. CUTICULAR PENETRATION

Exponential models of the uptake of DOG into bean are presented in Table 2. The high R<sup>2</sup> values (62 to 82%) indicate that an exponential time course for foliar uptake was a reasonable assumption, with the exception of the Silwet mixture. Without exception, these equations provided a better fit to the data than when the model was forced to fit the asymptote (the predicted maximum uptake) at 100% uptake. Since none of the asymptotes exceeded 50% uptake, it would clearly be wrong to assume that the foliar uptake process would necessarily continue until, effectively, all applied chemical was absorbed. It is customary, as in this report, to consider the proportion of chemical absorbed, i.e., uptake expressed as a percentage. This proportion depends on the rate of chemical application.<sup>27</sup> Application of

DOG at concentrations up to three orders of magnitude less than that reported resulted in models for uptake with increased asymptotes (data not presented). Nonetheless, those asymptotes did not approach 100% uptake. The asymptote was influenced by the surfactant (Table 2). Although Agral 90 had no effect, Triton X-45, Silwet L-7607, and the Silwet mixture all significantly increased the proportion of DOG that would ultimately be absorbed. The increase in asymptote on addition of both Triton X-45 and Silwet L-7607 was not associated with significant alterations of either the intercept (primarily influenced by stomatal infiltration) or the slope, i.e., rate of uptake. This implies that the enhancement of uptake provided by these two surfactants was attributable to an extension of the time period during which cuticular penetration proceeded. It is difficult to envisage any means by which this could be achieved other than an effect on the form of the chemical deposits on the leaf surface. Enhanced uptake of DOG into maize has been correlated with the hygroscopic water retention of Triton surfactants.<sup>26</sup> It appeared that the greater the amount of water retained by the surfactant, the greater was the proportion of chemical in solution and thus the greater the uptake. Agral 90 (mean EO 9) is expected to be more hygroscopic than Triton X-45 (mean EO 4.5); thus, an anomaly remains for the present data because Agral 90 had no significant effect on uptake, while Triton X-45 increased uptake 1.5-fold. However, the rate at which surfactant penetrates into the leaf may be much faster than the rate of penetration of DOG. Agral 90 may be taken up more rapidly than Triton X-45 and if so, DOG, when applied with Agral 90, may be left "high and dry" on the leaf surface sooner than when applied with Triton X-45. In the absence of surfactant and water (DOG is only very weakly hygroscopic<sup>26</sup>), DOG will crystallize, reducing uptake to a negligible rate.

Only mean uptake values have been quoted for the uptake of DOG in the presence of Silwets L-77 and Y-12301 and for the Silwet mixture when applied in the light (Table 2). In these cases, the slopes of the uptake models were not significantly different from zero, i.e., there was no statistical basis to assume that uptake continued to increase with increasing time postapplication. This was attributable to extremely high levels of variation associated with the stomatal infiltration provided by these surfactant solutions. Silwet L-7607 exhibited the range of variability of uptake (mean  $\pm$  10%) normal for studies of this type (Figure 2). In contrast, the variability encountered with Silwet L-77 was much greater (mean  $\pm$  30%). At application, infiltration of stomata was observed to vary markedly both among leaves and between areas of the same leaf. This was in accord with previous observations of stomatal variability.<sup>6,24,25</sup> Clearly, the variability encountered with these organosilicone surfactants was so great that increasing replication beyond the ten plants sampled at each time interval would have been of limited value. Instead, sampling at intervals later than 6 h postapplication was required to determine if there was a trend for uptake to increase with time. A 6-h time course was initially selected for this study because it is a widely accepted rule of thumb that rain falling within 6 h of application necessitates that a spray be reapplied. It is clear that use of Silwet L-77, providing a mean of 50% uptake of DOG into bean within 10 min (Figure 3), is likely to enable this critical period to be reduced to the droplet drying time.

Descriptors of uptake for applications made in the dark are tabulated only for the Silwet mixture and Silwets L-77 and Y-12301 (Table 2). For all other surfactants, uptake in the dark was not significantly different from that in the light with respect to either asymptote, intercept, or slope. These findings are in contrast to previous reports of stimulation of foliar uptake by light.<sup>8,21</sup> DOG is actively taken up by cells in a manner similar to that of glucose, requiring energetic phosphorylation.<sup>10</sup> This process will be favored by photosynthesis and should assist foliar uptake by maintaining the diffusion gradient across the cuticle. Therefore, although plants treated in the dark were without illumination for only the first 1.75 h on

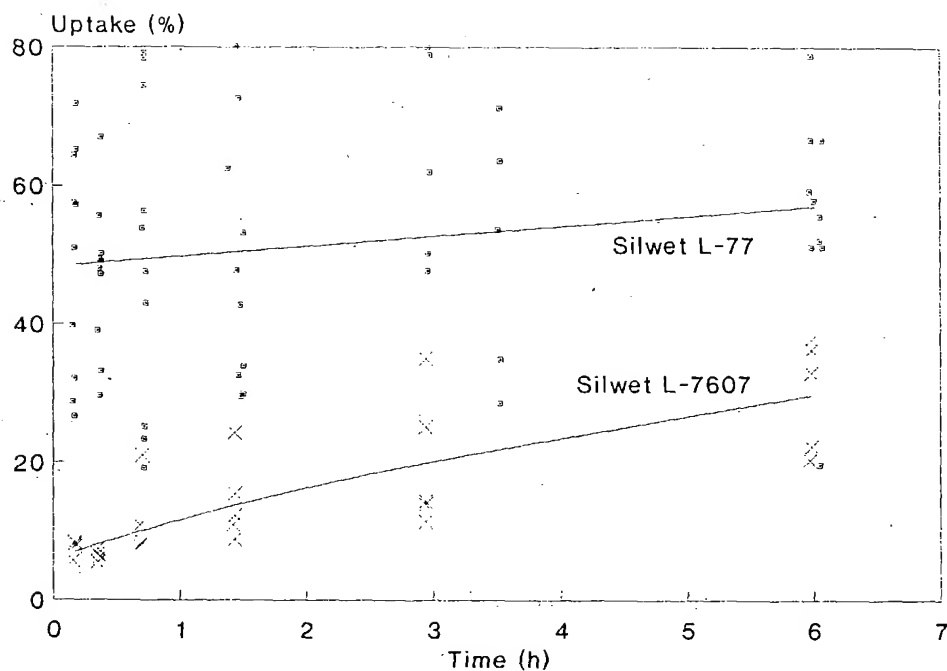


FIGURE 2. Effect of stomatal infiltration induced by Silwet organosilicone surfactants (0.5%) on variability of uptake of DOG into bean leaf in light.

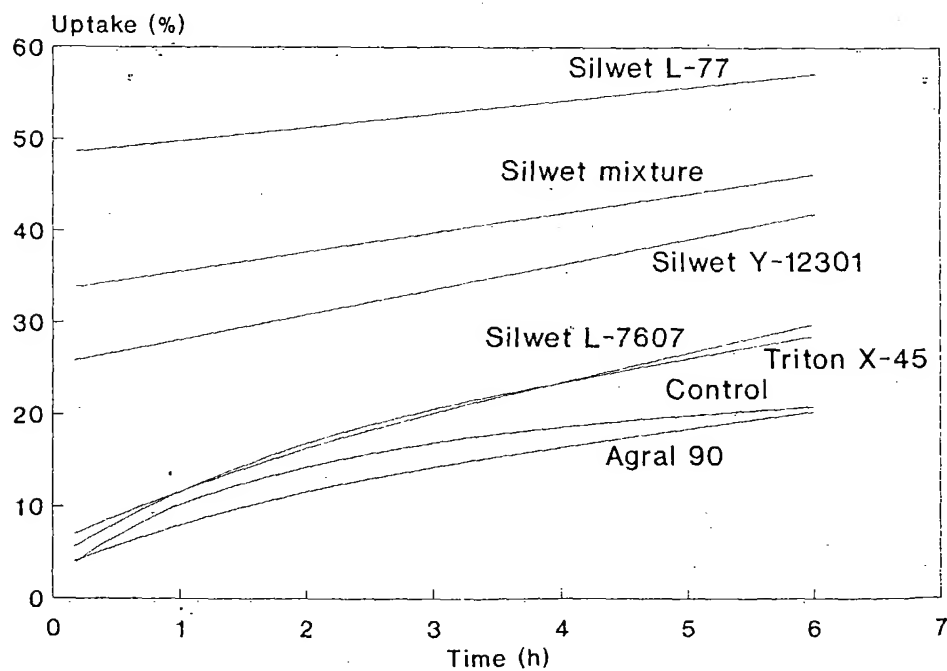


FIGURE 3. Effect of surfactants (0.5%) on time course of uptake of DOG into bean leaf in light.



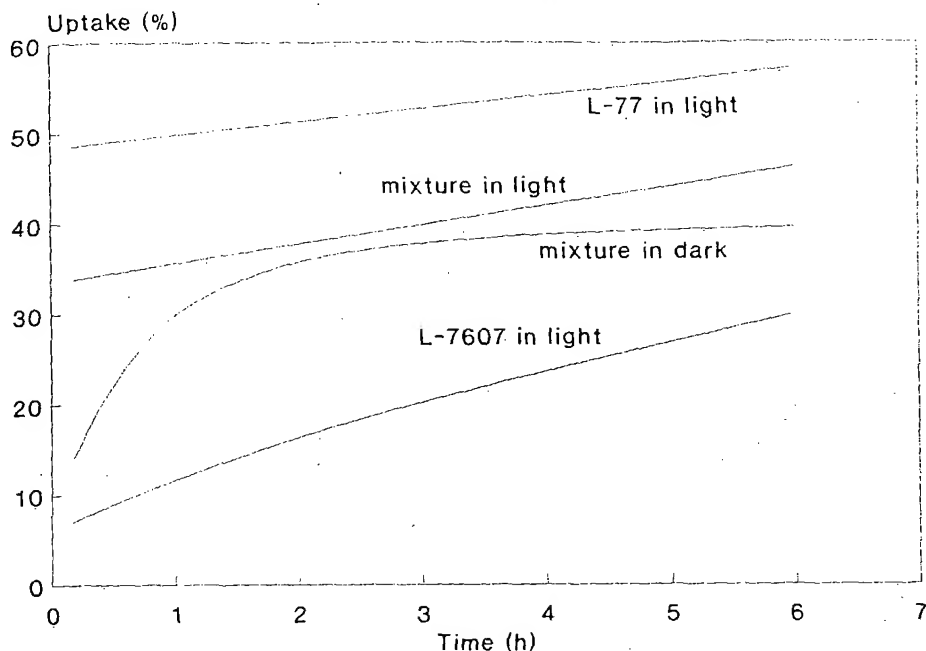


FIGURE 4. Effect of Silwet organosilicone surfactants (0.5%) on time course of uptake of DOG into bean leaf.

average, it was somewhat surprising to find no evidence for an effect of illumination on the uptake of DOG. Uptake in the presence of Silwets L-77 and Y-12301 when applied in the dark has already been discussed. The behavior of the Silwet mixture was most interesting, being intermediate between that of Silwets L-7607 and L-77. In the light, the mixture behaved in a manner akin to Silwet L-77, providing a relatively high-level (33%) of initial uptake by stomatal infiltration, but with a continuing increase in uptake by cuticular penetration that was not significant (Figure 4). In contrast, in the dark, the initial uptake afforded by the Silwet mixture was reduced threefold, but considerable subsequent cuticular penetration occurred. Interestingly, this penetration was at a rate significantly faster than that provided by Silwet L-7607 (Table 2).

The effects of Silwet L-77 on uptake were dependent on concentration (Table 3). The intercept for the model of uptake in the presence of 0.1% Silwet L-77 (12%) provided no evidence for stomatal infiltration (Table 1). The intercept for 0.2% Silwet L-77 was slightly elevated (17%), suggesting that this was at or about the threshold concentration required to induce infiltration. Although both of the lower concentrations of Silwet L-77 significantly increased the uptake asymptote relative to the control (Table 2), this was not achieved by an increase in the rate of penetration. It was notable that the proportion of DOG ultimately taken up varied little between concentrations (Table 3). However, as a result of stomatal infiltration, Silwet L-77 at 0.5% provided levels of uptake (51%) within 10 min of application equivalent to those achieved by solutions incorporating 0.1 and 0.2% after more than 30 h (43 and 50%, respectively).

There was no evidence that the substitution of glyphosate monoisopropylamine for DOG as the a.i. had any effect on the kinetics of uptake (Table 4). Uptake remained primarily a process of stomatal infiltration, 51% of a total of 65% of glyphosate ultimately absorbed being taken up within a few minutes of application. The establishment of an exponential model for the uptake of glyphosate, in contrast to DOG, was simply the result of uptake



TABLE 3  
Effect of Silwet® L-77 Concentration on Time Course of Uptake of Deoxyglucose into Bean Leaf in the Light

Conc (% w/v)	% Uptake = $A - (B \times S^{\text{Time in h}})$			Coefficient of determination ( $R^2$ as %)
	Asymptote (A)	Intercept (A - B)	Slope (S)	
0.1 <sup>a</sup>	43 a	12 d	0.92 a	84
0.2 <sup>a</sup>	50 ab	17 c	0.95 b	69
0.5 <sup>b</sup>		51 <sup>c</sup> b	NS	

Note: Within columns, treatments with letters in common are not significantly different at  $p = 0.05$ ; asymptotes may be compared with intercepts. NS, not significant (i.e., no significant increase in uptake with time).

<sup>a</sup> Time course: 10 min-45 h postapplication.

<sup>b</sup> Time course: 10 min-6 h postapplication.

<sup>c</sup> Mean uptake for all samples, regardless of time.

TABLE 4  
Effect of Active Ingredient and Formulation on Uptake into Bean Leaf in Light in Presence of Silwet L-77 (0.5%)

Chemical	% Uptake = $A - (B \times S^{\text{Time in h}})$			Coefficient of determination ( $R^2$ as %)
	Asymptote	Intercept (A - B)	Slope	
Deoxyglucose <sup>a</sup>		51 <sup>d</sup> c	NS	
Glyphosate monoisopropylamine <sup>b</sup>	65 a	51 c	0.15 a	11
Roundup <sup>c</sup>	77 b	37 d	0.91 b	45

Note: Within columns, treatments with letters in common are not significantly different at  $p = 0.05$ ; asymptotes may be compared with intercepts. NS, not significant (i.e., no significant increase in uptake with time.)

<sup>a</sup> Time course: 10 min to 6-h postapplication.

<sup>b</sup> Time course: 10 min to 22-h postapplication.

<sup>c</sup> Time course: 10 min to 45-h postapplication.

<sup>d</sup> Mean uptake for all samples, regardless of time.

determinations being extended to 22-h postapplication. The variability inherent in the data (Figure 2) resulted in a poor fit of the model to the data ( $R^2 = 11\%$ ). A better-fitting model ( $R^2 = 45\%$ ) was established for the time course of uptake of Roundup, which was extended to 45h postapplication. The intercept, i.e., stomatal infiltration, was significantly reduced with Roundup. This was a result of antagonism between the Silwet L-77 and the surfactants in the Roundup formulation, an effect readily visualized as a reduction in contact angle and spreading on the leaf surface. The data for Roundup illustrate that the apparent absence of any effect of Silwet L-77 on cuticular penetration is unlikely to be of concern in commercial practice. Silwet L-77 is utilized as an adjuvant with Roundup, not as a formulant, and this organosilicone surfactant can provide high levels of uptake almost instantaneously via infiltration of stomata while the a.i.'s formulants can then ensure continuing uptake. The potential value of Silwet L-77 is illustrated by the fact that only 77% of the Roundup was absorbed over 40 h after application, and that level of uptake was achieved only with the aid of 37% stomatal infiltration provided by Silwet L-77.

TABLE 5  
Effect of Surfactant (0.5%) on Time Course (10 min to 22-h  
Postapplication) on Uptake of Deoxyglucose into Oat and Winter Wheat  
Leaves in Light

Species	Surfactant	% Uptake = $A - (B \times S^{\text{Time in h}})$			Coefficient of determination (R <sup>2</sup> as %)
		Asymptote (A)	Intercept (A - B)	Slope (S)	
Oat	Agral 90	91 a	15 a	0.66 a	93
	Silwet L-7607	87 b	30 b	0.83 b	88
	Silwet L-77	64 c	35 c	0.62 a	81
Winter wheat	Agral 90	97 a	-8.1 a	0.31 a	98
	Silwet L-7607	89 b	21 a	0.8 b	97
	Silwet L-77	66 c	22 c	0.51 c	94

Note: Within columns, treatments with letters in common are not significantly different at  $p = 0.05$ ; asymptotes may be compared with intercepts.

The effects of Agral 90 and Silwets L-7607 and L-77 on uptake into the grass species, oat, and winter wheat were reversed relative to bean (Table 5). Silwet L-7607 appeared to induce stomatal infiltration to only a slightly lesser extent than Silwet L-77. However the continuing cuticular penetration in the presence of Silwet L-7607 was greater than that provided by Silwet L-77, such that uptake with Silwet L-77 was exceeded by Silwet L-7607 approximately 4 h after application to both grass species (Figure 5). It remains uncertain if the effect of these surfactants was an enhancement of the rate of cuticular penetration because the hydrophobic nature of the leaf surfaces of these grasses prevented application of purely aqueous solutions as a control treatment. Agral 90 had no significant effect on uptake into bean. In contrast, the rate of cuticular penetration provided by Agral 90 into oat and wheat was so rapid that the advantage of the stomatal infiltration provided by Silwet L-77 was overtaken after 1.5 h in oat and only 0.75 h in winter wheat. Agral 90 was also notable in these species as the only treatment for which uptake approached 100%. Despite the lower asymptotes for Silwet L-7607 and particularly for Silwet L-77, the high R<sup>2</sup> values (81 to 97%) indicated that uptake did follow exponential time courses. Clearly, the nature of the target species should be considered when selecting a spray adjuvant.

### C. TRANSLOCATION

Since the majority of modern agrichemicals are active systemically in plants, it would be inappropriate to consider the effects of spray adjuvants on foliar uptake in isolation of their effects on translocation. Considerable quantities of surfactants may enter the leaf tissues directly by cuticular penetration<sup>23</sup> or, as evidenced by the organosilicone surfactants in the present study, indirectly via infiltration of the stomatal pores. The phytotoxicity of surfactants, primarily mediated by their disruption of membranes, is well established<sup>17</sup> and may be manifested as deleterious effects on translocation.<sup>5</sup> However, in the current study, translocation of DOG in bean was significantly enhanced by Silwet L-77, in contrast to the other surfactants tested (Table 6). This result was in accord with the low phytotoxicity of Silwet L-77 as measured by ethylene production by leaves of bean<sup>29</sup> and by ion and pigment leakage studies.<sup>2</sup>

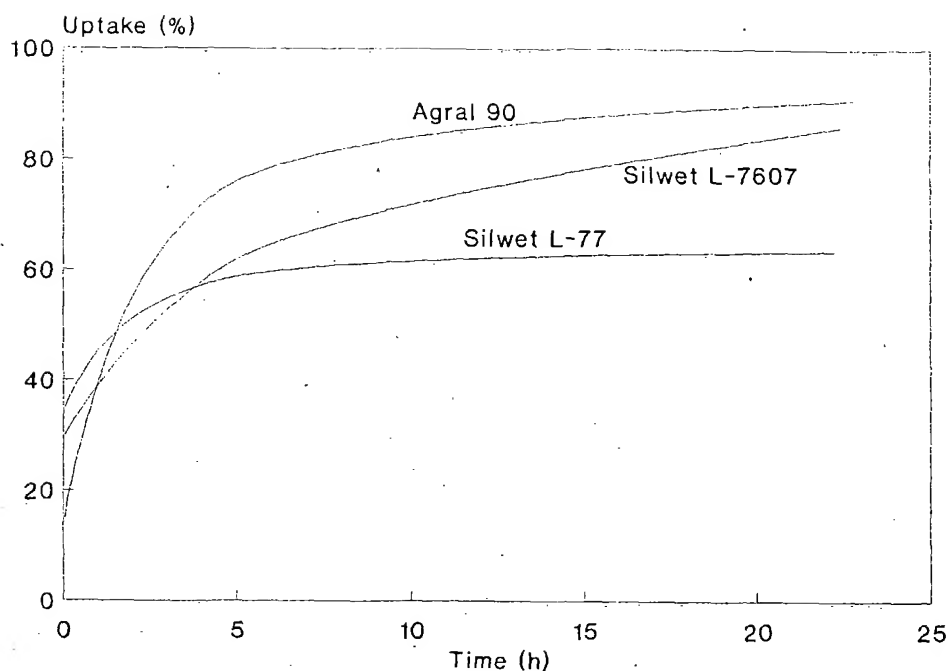


FIGURE 5. Effect of surfactants (0.5%) on time course of uptake of DOG into oat leaf in light.

TABLE 6  
Effect of Surfactant (0.5%) on  
Translocation of Deoxyglucose Out  
of Treated Leaflet of Bean 6-h  
Postapplication

Treatment	Translocation (% of applied $^{14}\text{C}$ )
Control (no surfactant)	6 bc
Agral 90	8 b
Triton X-45	4 c
Silwet L-7607	3 c
Silwet L-77	14 a

Note: Treatments with letters in common are not significantly different at  $p = 0.05$ .

#### IV. CONCLUSIONS

It is apparent that high levels of foliar uptake can be achieved almost instantaneously by utilizing Silwet L-77 as a spray adjuvant to induce stomatal infiltration. Although other organosilicone surfactants also have this ability, none of those studied provided such high levels of uptake via infiltration and all were attenuated to a greater extent by partial stomatal closure than was Silwet L-77. Stomatal infiltration by Silwet L-77 required concentrations in excess of 0.2% and enhanced the translocation of the a.i. On the basis of the present studies, it appears that the ability of surfactants to induce stomatal infiltration is largely exclusive of an ability to enhance cuticular penetration, with the exception of a mixture of

Silwets L-77 and L-7607. Surfactant enhancements of foliar uptake via the latter pathway may be mediated by an increased rate of penetration and/or more commonly by an increase in the proportion of the a.i. ultimately taken up. The effects of surfactants on foliar uptake are species specific.

## ACKNOWLEDGMENTS

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## Chapter 37

## SPRAY FORMULATION WITH SILWET® ORGANOSILICONE SURFACTANTS

Paul J. G. Stevens, Jerzy A. Zabkiewicz, Jonathan H. Barran, K. R. Klitscher, and  
Fiona Ede

The potential of organosilicone surfactants as adjuvants for herbicides was reported as early as 1973. During the mid-1970s, the advantages of incorporating Silwet L-77 into sprays to alleviate iron chlorosis in citrus were reported from Israel. No further reports appeared until the mid-1980s. Since then, more than 70 papers, mostly originating in New Zealand, have reported the properties of Silwet surfactants and their utility as spray adjuvants. Silwet L-77 is now widely used as a spray adjuvant in New Zealand, with increasing use in Australia and Southeast Asia. It is also being introduced in the U.S. and elsewhere. The literature on organosilicone surfactants relates predominantly to herbicides, largely reflecting the commercial development of Silwet L-77 to assist scrubweed control in New Zealand forestry. However, this surfactant has also been used effectively with growth regulators, foliar nutrients, and an insecticide.

The videofilm presented at this symposium demonstrates the unusual properties of organosilicone surfactants and illustrates the dynamic behavior of solutions which enhance the utility of sprays formulated with Silwets:

1. The leaf wetting and spreading capabilities of Silwets far surpass those of "conventional" surfactants.
2. The exceptionally low aqueous surface tensions produced by Silwet L-77 enable spray liquids to infiltrate stomata, enhancing uptake of the active ingredient and making the pesticide taken up in this manner immediately rainfast.
3. The Silwets have low phytotoxicity and are thus relatively less deleterious to the translocation, and hence systemic activity, of pesticides than many other surfactants.

This videofilm is available for loan from the authors.\* The following references on Silwet organosilicone surfactants in agriculture documents the properties and behavior illustrated in the videofilm.

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## Chapter 38

**EFFECT OF PLANT AGE AND ADJUVANT ON THE FOLIAR  
PENETRATION AND TRANSLOCATION OF GLYPHOSATE IN  
PAMPAS GRASS (*CORTADERIA SELLOANA*)**

Robyn E. Gaskin and Jerzy A. Zabkiewicz

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## ABSTRACT

The addition of a nonionic surfactant, Silwet® L-77, enhanced the uptake of  $^{14}\text{C}$ -glyphosate into pampas grass foliage. Uptake decreased with plant age for all treatments, but the relative enhancement was greatest with oldest plants. Addition of surfactant decreased translocation of the herbicide in the youngest plants, while increasing it in the oldest plants. Phytotoxicity of the herbicide formulation, both visible and measured, was greatest in the youngest tissues and enhanced in the presence of surfactant. The translocation characteristics are considered to be a consequence of the phytotoxicity of the different formulations. The severity of phytotoxicity was inversely related to the foliage age.

## I. INTRODUCTION

Pampas grass (*Cortaderia* spp.) has emerged as a serious forest weed problem in New Zealand in recent years. This has brought about major studies of its biology<sup>4,6</sup> and options for its chemical control.<sup>3,8</sup> Glyphosate was one of the herbicides investigated, but was found to be relatively ineffective against mature plants unless adjuvants, usually nonionic surfactants, were added to the spray. The need for adjuvants with glyphosate sprays has been recognized for some time, especially for the control of grasses.<sup>1,10</sup> Not only is spray efficacy increased, but more consistent control is obtained throughout a growing season. An adjuvant that is particularly effective with glyphosate is Silwet L-77, a nonionic organosilicone surfactant.<sup>11</sup> Silwet L-77 has the ability to reduce spray solution surface tensions to approximately 20 to 22 mN m<sup>-1</sup>, which ensures excellent wetting of the leaf surface.<sup>14</sup> Glyphosate uptake and translocation in pampas grass was investigated to determine if efficacy could be improved by the addition of Silwet L-77. An initial study<sup>5</sup> had shown that there was enhancement of herbicide uptake into pampas grass with adjuvant addition, but that there was a corresponding decrease in translocation of herbicide (absorbed) out of the treated leaves. Such an effect could result in reduced field efficacy, the opposite of the desired result. During this earlier study, it was noted that the phytotoxicity of the spray solution was much greater when it contained both herbicide and surfactant, compared to the herbicide with no added surfactant. The foliage treated in the first study was young (1 month old) and severe leaf necrosis was noted at the site of application. The lack of significant improvement with adjuvant addition, together with the phytotoxicity, indicated undesirable effects occurring with this spray formulation at this growth stage. Accordingly, further work was undertaken to elucidate the effect of adjuvant addition to glyphosate on pampas grass foliage of varying age. The results, presented in comparison with the earlier results, form the content of this chapter.

## II. MATERIALS AND METHODS

The work was undertaken on pampas grass (*Cortaderia selloana*) foliage of three different ages. The 1-month-old foliage was raised and treated as described by Gaskin and Murray.<sup>5</sup> The 4- and 6-month-old foliage was grown in a greenhouse using commercially obtained pampas grass seedlings (Massey strain). They were transferred to a controlled environment room (24/17°C day/night temperature, 70% relative humidity [RH], 14-h photoperiod, 500  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) for 3 weeks prior to treatment. Plants were actively growing at the time of treatment. Water was supplied as required and fertilizer (Response Black Label 9-4-6®, Growth Marketing; 0.2%, v/v) was applied weekly.

Glyphosate (as Roundup® at 33 ml l<sup>-1</sup> water) was applied alone or in combination with the nonionic organosilicone surfactant Silwet L-77 (silicone polyalkyleneoxide copolymer,

Union Carbide) at either 0.1 or 0.2% (v/v).  $^{14}\text{C}$ -glyphosate (Amersham, 98.3% purity) was formulated as the monoisopropylamine salt and incorporated in the treatment formulation ( $0.2 \mu\text{Ci ml}^{-1}$ ). Ten  $0.5\text{-}\mu\text{l}$  droplets were applied by microsyringe to each adaxial and abaxial surface over the middle 5-cm length of the selected leaf (4 or 6 months old, four plant replicates). Equivalent droplets of treatment solution were dispensed into scintillation vials to determine the dose of  $^{14}\text{C}$ -glyphosate applied to the plants.

Five days after application, the treated leaf was excised and the treated portion washed to remove unabsorbed herbicide residues.<sup>5</sup> The radioactivity within the treated leaf portion was determined by oxidizing finely ground (Wiley mill) subsamples of homogeneous tissue from this treated portion (approximately 10 mg) in a Micromat BF 5010 oxidizer, after freeze drying and weighing the foliage. All tissue samples were analyzed in triplicate and the solutions (5.5 g of Permablend I®, Parkard, IL, plus 150 ml of methanol  $1^{-1}$  of toluene) radioassayed in a Packard 4430 liquid scintillation counter. The total radioactivity within the tissue was calculated by scaling up to total tissue dry weight; previous work<sup>5</sup> had confirmed  $^{14}\text{C}$ -glyphosate recoveries of greater than 81% (mean 86%).

Uptake was expressed as a percentage of the radioactivity applied. Translocation was calculated as the radioactivity which was not recovered in the washes or by oxidation of the treated tissue, and expressed as a percentage of both  $^{14}\text{C}$ -glyphosate absorbed by, and applied to, the plant. Phytotoxicity was quantified as electrolyte leakage (% conductivity) from pampas grass leaves after immersion in the treatment solutions for 24 h.<sup>5</sup> All treatment results were tested by analysis of variance and the means compared by the least significant difference (LSD) test.

### III. RESULTS

The results from the  $^{14}\text{C}$ -glyphosate uptake and translocation studies, and those from the formulation phytotoxicity tests, are presented in Table 1.

The addition of Silwet L-77 enhanced uptake significantly only in the treatment of foliage aged 6 months. The translocation (of  $^{14}\text{C}$  absorbed) out of the treated leaf portions was significantly reduced in the youngest, unchanged in the 4-month-old, and increased (at the highest rate) in the 6-month-old foliage by the addition of surfactant. Consequently, the translocation of glyphosate (as a percentage of  $^{14}\text{C}$  applied) in the oldest foliage was significantly greater with solutions containing surfactant.

The conductivity data, used as an indicator of phytotoxicity, also showed trends related to formulation and plant age. Electrolyte leakage decreased significantly with increasing foliage age in all adjuvant treatments. Addition of surfactant to the glyphosate formulation resulted in increased electrolyte leakage. This was significant in 4-month-old foliage at both rates of addition and in 6-month-old foliage at the higher rate.

### IV. DISCUSSION

Roundup contains surfactants. However, differences exist in the control of different weed species by glyphosate. The variations in control have frequently been attributed to differences in uptake, and a wide range of surfactant adjuvants have been tested with the aim of improving absorption of the chemical, and hence field efficacy. Such work demonstrated that surfactants can either enhance or antagonize glyphosate activity.<sup>13</sup> Leaf tissue necrosis and cell membrane damage have been suggested as factors which reduce the efficacy of the herbicide.<sup>7,9</sup>

The initial study of  $^{14}\text{C}$ -glyphosate uptake and translocation in pampas grass demonstrated that nonionic surfactants could enhance uptake.<sup>5</sup> This result was confirmed in the present

TABLE 1  
Uptake, Translocation, and Phytotoxicity of Glyphosate  $\pm$  Silwet L-77  
in Pampas Grass of Differing Ages

Treatment	Plant age (months)	%	% Translocation		Conductivity (%)
			Uptake of $^{14}\text{C}$	Absorbed $^{14}\text{C}$	Applied $^{14}\text{C}$
Glyphosate	1 <sup>a</sup>	88.4 a	45.5 c	40.3 bc	25.5 c
+0.1% L-77	1 <sup>a</sup>	94.0 a	20.8 d	19.6 d	75.5 a
+0.2% L-77	1 <sup>a</sup>	94.6 a	20.9 d	19.8 d	80.8 a
Glyphosate	4	54.9 c	92.3 a	50.8 ab	16.6 cd
+0.1% L-77	4	60.2 bc	91.2 a	54.9 ab	40.7 b
+0.2% L-77	4	61.0 bc	92.4 a	56.4 a	40.6 b
Glyphosate	6	32.5 d	78.1 b	26.8 cd	10.6 d
+0.1% L-77	6	70.9 b	86.2 ab	61.5 a	21.0 cd
+0.2% L-77	6	64.9 bc	90.0 a	58.5 a	25.9 c

Note: Column means sharing common postscripts are not significantly different at the 5% level (LSD test). Glyphosate as Roundup (Monsanto) at 3.33% (v/v).

<sup>a</sup> Data from Reference 5.

study. Although the improvements were minor at 1 and 4 months, significant enhancements occurred in 6-month old foliage. Uptake of glyphosate decreased with increasing foliage age; thus, the relative enhancement with the addition of Silwet L-77 was greatest in the oldest tissues.

In the youngest leaves (1 month old), there was a significant reduction in translocation when Silwet L-77 was added to the formulation. No difference was obtained with 4-month-old foliage, and there was significant enhancement of translocation in the 6-month-old foliage with addition of 0.2% Silwet L-77.

A similar trend was observed in the percentage of applied glyphosate translocated. Translocation of  $^{14}\text{C}$ -glyphosate was reduced in the youngest foliage in the presence of the surfactant; no difference was observed between treatments applied to the 4-month-old leaves, and significant enhancement of translocation occurred in 6-month-old foliage with the addition of Silwet L-77.

These results demonstrate that, even taking into account the general decline in uptake with increasing leaf age, the controlling factor in the efficacy of these treatments will probably be the translocation behavior of the glyphosate. It was also observed that the youngest leaves developed necrotic lesions (contact phytotoxicity) after treatment with glyphosate plus surfactant. Electrolyte leakage has been used as a quantitative indicator of herbicide or formulation damage.<sup>2,7,12</sup> It has been found<sup>5</sup> that surfactant solutions caused little electrolyte leakage from pampas grass foliage; neither did the glyphosate spray solution. However, addition of surfactant to the glyphosate spray increased electrolyte leakage two- to threefold. The amount varied with foliage age, from 26% in six-month-old foliage to 81% leakage in the 1-month-old foliage. The percentage conductivity was inversely correlated with translocation ( $R^2 = 0.59$ ,  $p = 0.009$ ), implying that increased electrolyte leakage resulted in decreased translocation.

It is clear that the age of pampas grass foliage can play a critical role in determining the effectiveness of glyphosate spray formulations. The extent to which translocation occurs will be affected by cell membrane integrity. A small increase in cell membrane permeability may improve short-distance transport and hence phloem loading, and result in improved translocation of the herbicide to the sinks. Loss of membrane integrity may reduce trans-



location, increase localized concentrations of the active ingredient, and result in localized cell death (contact phytotoxicity) and, thus, reduced herbicide performance. This is particularly important in the case of perennial, rhizomatous or woody weeds, as regrowth can occur from roots and long-term control will be reduced.

## V. CONCLUSIONS

Addition of Silwet L-77 to glyphosate may enhance its effectiveness on pampas grass, as demonstrated by some increased uptake of the formulation, regardless of leaf age. Proportionately, the gains are greatest with the oldest plants, as uptake decreased with foliage age. Addition of surfactants to glyphosate formulations caused the greatest phytotoxicity in young foliage, and this reduced translocation. Mature foliage showed no visible or measurable evidence of excessive phytotoxicity, and under these circumstances, surfactant addition is expected to significantly increase herbicide effectiveness.

## ACKNOWLEDGMENT

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## Chapter 39

**COMPARISON OF STATISTICAL METHODS FOR EVALUATING  
SILICONE ADJUVANTS FOR NA-ACIFLUORFEN**

Frank C. Roggenbuck, Loston Rowe, Donald Penner, Richard Burow,  
Robert Ekeland, and Len Petroff

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## ABSTRACT

Silicone surfactants have recently been identified as providing increased efficacy and rainfastness for the herbicide Na-acifluorfen [5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid] on velvetleaf (*Abutilon theophrasti* Medic.). The objectives of this study were to compare two statistical methods for determining the Na-acifluorfen application rate, identifying the most effective adjuvant, and selecting the application rate of this adjuvant necessary to provide velvetleaf control. The greenhouse study was done with and without simulated rainfall to evaluate rainfastness.

Use of the Box-Behnken design and analysis of data required only 15 treatments, compared to the 27 treatments required by a three-way factorial design and analysis. Both statistical methods identified similar treatment response trends and facilitated the identification of the most effective adjuvant treatment.

## I. INTRODUCTION

The Weed Science Society of America defines an adjuvant as "any substance in a herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics".<sup>8</sup> The control of velvetleaf with Na-acifluorfen, especially under low relative humidity, is often less than desired.<sup>6,9</sup> Various adjuvants have been shown to be useful in increasing Na-acifluorfen activity for velvetleaf.<sup>7,9</sup> Furthermore, silicone adjuvants have been shown to increase herbicide rainfastness.<sup>4,7</sup> A 6-h rain-free period after Na-acifluorfen application is considered necessary for expression of maximum activity. The rain-free periods required by various herbicides for johnsongrass (*Sorghum halepense* (L.) Pers.) have been documented by Bryson.<sup>2,3</sup>

As early as 1973, Jansen<sup>5</sup> reported on the potential of silicone adjuvants for increasing herbicide activity. Recent reports on the efficacy of the silicone adjuvants for rainfastness<sup>4,7</sup> provide evidence for the need of identifying silicone adjuvants that will provide maximum economic increase in the efficacy and rainfastness of a specific herbicide.

The objectives of this study were to compare two statistical methods for determining (1) the Na-acifluorfen application rate, (2) the most effective silicone adjuvant in a series, and (3) the most effective application rate of this adjuvant necessary to provide velvetleaf control.

## II. MATERIALS AND METHODS

Velvetleaf seeds were placed in 0.946-l plastic cups filled with a BACCTO® professional potting mix. These were placed in a greenhouse at  $25 \pm 2^\circ\text{C}$ , with an 18-h day and 6-h night with supplemental lighting to provide  $1200 \mu\text{E m}^{-2} \text{s}^{-1}$ . After emergence, the plants were thinned to one plant per cup and watered as needed. Herbicide treatments were made after 21 d when the velvetleaf plants were in the five-leaf stage and 13 cm tall.

To facilitate the evaluation of the adjuvants, the herbicide and silicone adjuvants were applied at rates bracketing the mid-level of velvetleaf visual injury. Adjuvant activity is most accurately evaluated at this mid-level of herbicide injury. Na-acifluorfen was applied at 0.017, 0.034, and 0.051 kg/ha, representing 0.5x, 1x, and 1.5x rates for the series. The highest rate approximates 10% of the label rate. The experimental silicone adjuvants were applied at 439, 877, and 1315 ml/ha, representing 0.5x, 1x, and 1.5x rates. The adjuvants selected for this study, A, B, and C, were three silicone adjuvants in a structural series. For the control study, crop oil concentrate was applied at 2339 ml/ha. The spray volume was 234 l/ha and the application pressure was 173 kPa.

TABLE 1  
Comparison of Treatments  
Required by Factorial Vs. Box-  
Behnken Design for Different  
Number of Factors

Factors	Number of treatments required	
	Factorial design	Box-Behnken design
2	9	—
3	27	15
4	81	27
5	243	46
6	729	54

To evaluate rainfastness, the plant received 2.54 cm of simulated rainfall in a 5-min period 15 min after the herbicide application. The velvetleaf plants were evaluated for visual injury 7 d after herbicide application. The data presented are the means of two experiments with four replications each.

The data were analyzed by analysis of variance (ANOVA) as a three-way factorial design using Duncan's multiple range test for mean separation. A subset of the treatments fulfilled the requirements of the Box-Behnken<sup>1</sup> design for multivariate analysis. The Box-Behnken design requires fewer treatments to economize screening costs, as shown in Table 1. The selection of treatments included in the Box-Behnken design relative to a factorial design is shown in Figure 1. A correlation analysis was done using both designs.

### III. RESULTS AND DISCUSSION

Even though a silicone adjuvant has been identified that is superior to crop oil concentrate for increasing the efficacy and rainfastness of Na-acifluorfen on velvetleaf (Table 2), additional research is required to optimize the activity within an analysis series of silicone adjuvants. Determination of the herbicide and adjuvant dosage to obtain maximum weed control is also critical in the evaluation or identification of appropriate adjuvants. A logical, traditional experimental design for this type of research is a three-way factorial, as shown in Table 3. If the research needs are extensive, the number of treatments required can prove costly and time consuming. The Box-Behnken design (Figure 1) requires fewer treatments, but opens the question of whether this design is adequate for adjuvant studies.

The data obtained in the absence of the simulated rain (Table 3) using a full three-way factorial design indicated that increased visual injury to velvetleaf was observed with increasing Na-acifluorfen rate, increasing adjuvant rate, and shifting from adjuvant A → B → C. The interaction term in the ANOVA was not significant and the main effect values clearly indicate the trends stated above. For plants receiving the simulated rain, the conclusions are similar except that adjuvant B was equal to C, and at the highest Na-acifluorfen and adjuvant application rate, adjuvant B was superior to adjuvant C (Table 3). Bryson<sup>3</sup> states that as herbicide rates decrease, the effects of rainfall increase. In this study, the rates of Na-acifluorfen used were much lower than those used in our previous report.<sup>7</sup> Thus, the extent of rainfastness was reduced. Silicone adjuvant C is a very effective adjuvant with Na-acifluorfen. At the highest rates of each, which for the Na-acifluorfen is 10% of the label rate, the velvetleaf injury was a very acceptable 89%.

The response surfaces for the full factorial and Box-Behnken designs for Na-acifluorfen rates of 0.017, 0.034, and 0.051 kg/ha without rain are shown in Figures 2 through 4,

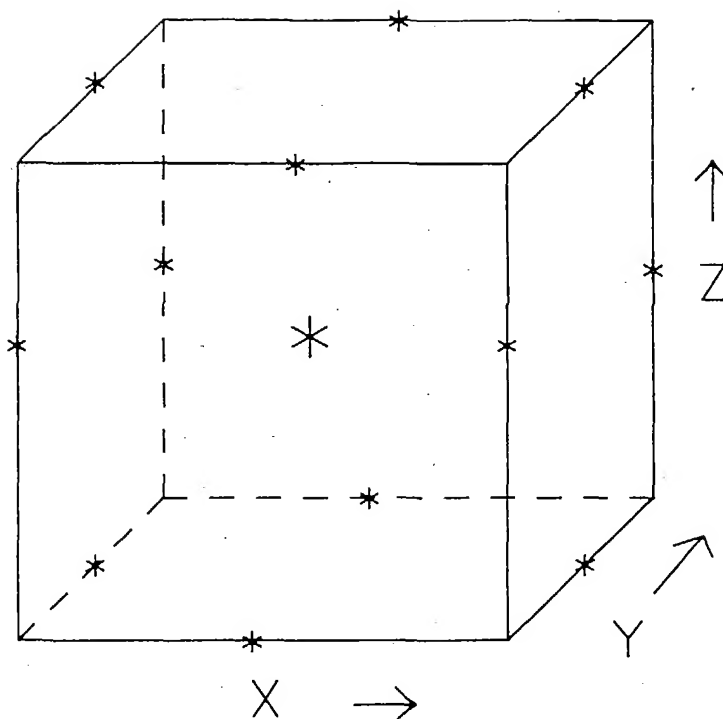


FIGURE 1. Relative location of treatments required by the Box-Behnken design for three factors, including three treatments at the center.

TABLE 2  
Comparison of a Silicone-Based  
Adjuvant with Crop Oil Concentrate on  
Na-Acifluorfen Efficacy on Velvetleaf

Treatment	Visual injury (%)	
	No rain	Rain
Control	0	0
Na-acifluorfen (0.034 kg/ha) + COC <sup>a</sup> (2.4 l/ha)	16	0
Na-acifluorfen (0.034 kg/ha) + adjuvant b (0.877 l/ha)	66	30

<sup>a</sup> COC, Herbimax<sup>®</sup> crop oil concentrate.

respectively. As expected, any differences between the response surface from the factorial and the Box-Behnken are most evident at the corners or limits of the response surface. However, these differences are not large. The response surfaces clearly indicate the extent of the activity lost with the rainfall treatment in Figure 5. The factorial and Box-Behnken designs show similar response surfaces for the rainfall treatments (Figure 6). The trends evident from Table 3 are apparent in Figures 2 through 6. A correlation analysis for the two designs indicates that within a given experiment, the  $R^2$  values are very similar for the two designs (Table 4); however, when the experiments are combined, the  $R^2$  values are lower for the Box-Behnken. Conclusions apparent from the surface responses obtained by either

TABLE 3  
Evaluation of Silicone Adjuvants with Varying Rates of Na-Acifluorfen on Injury to Velvetleaf in the Presence or Absence of Rain Using ANOVA

Treatments			Visual injury (%)*	
Na-acifluorfen rate (kg/ha)	Surfactant	Surfactant rate (ml/ha)	No rain	Rain
0.017	A	439	8 l	1 m
		877	11 kl	9 j-m
		1315	36 g-i	10 j-m
	B	439	21 j-k	15 i-l
		877	41 f-h	18 g-l
		1315	50 e-f	21 f-j
	C	439	29 i-j	19 g-k
		877	50 e-f	20 g-j
		1315	58 d-e	25 e-i
0.034	A	439	10 l	5 l-m
		877	28 i-j	14 i-m
		1315	39 f-i	14 i-m
	B	439	41 f-h	10 j-m
		877	66 c-d	30 c-g
		1315	69 b-c	35 c-e
	C	439	35 g-i	16 h-l
		877	83 a	34 c-f
		1315	84 a	43 b-c
0.051	A	439	10 l	6 k-m
		877	34 h-i	16 h-l
		1315	49 e-f	21 f-j
	B	439	41 f-h	15 i-l
		877	78 a-b	51 a-b
		1315	83 a	61 a
	C	439	46 e-g	29 d-h
		877	84 a	40 b-d
		1315	89 a	42 b-c
Main Effect				
0.017			34 c	15 c
0.034			51 b	22 b
0.051			57 a	31 a
	A		25 c	11 b
	B		55 b	28 a
	C		62 a	30 a
		439	27 c	13 c
		877	53 b	26 b
		1315	62 a	30 a

Note: Numbers presented are the means of two experiments with four replications per experiment.

Means followed by the same letter within a column are not significantly different at the 5% level according to Duncan's multiple range test.



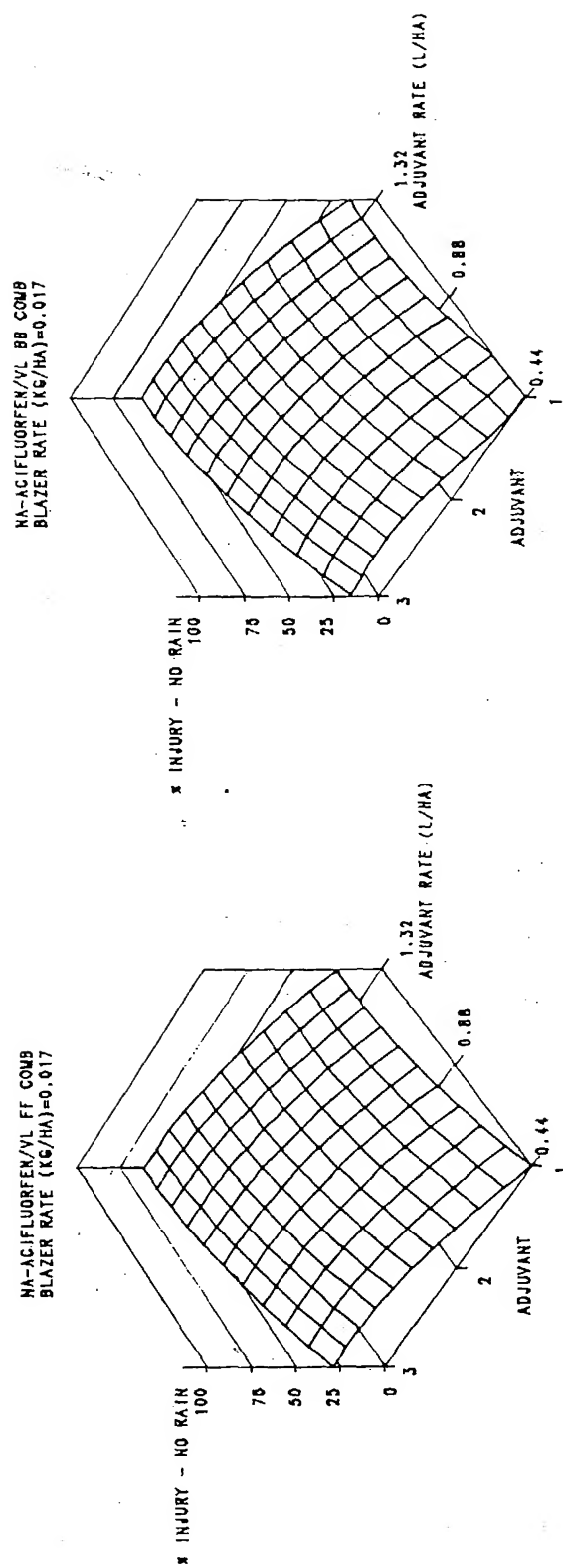


FIGURE 2. Response surfaces for factorial (left) and Box-Behnken (right) designs for the no-rain treatment with Na-acifluorfen applied at 0.017 kg/ha. Adjuvants 1, 2, and 3 correspond to adjuvants A, B, and C, respectively (see text).

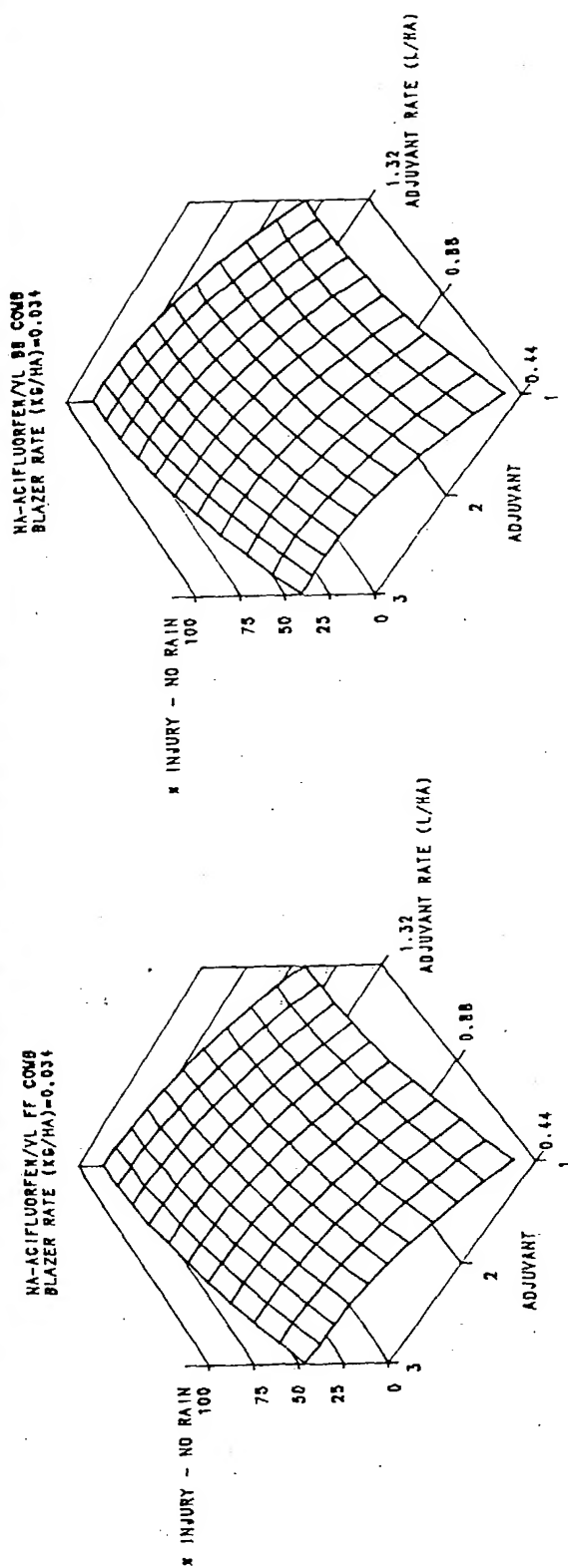


FIGURE 3. Response surfaces for factorial (left) and Box-Behnken (right) designs for the no-rain treatment with Na-acifluorfen applied at 0.034 kg/ha. Adjuvants 1, 2, and 3 correspond to adjuvants A, B, and C, respectively (see text).

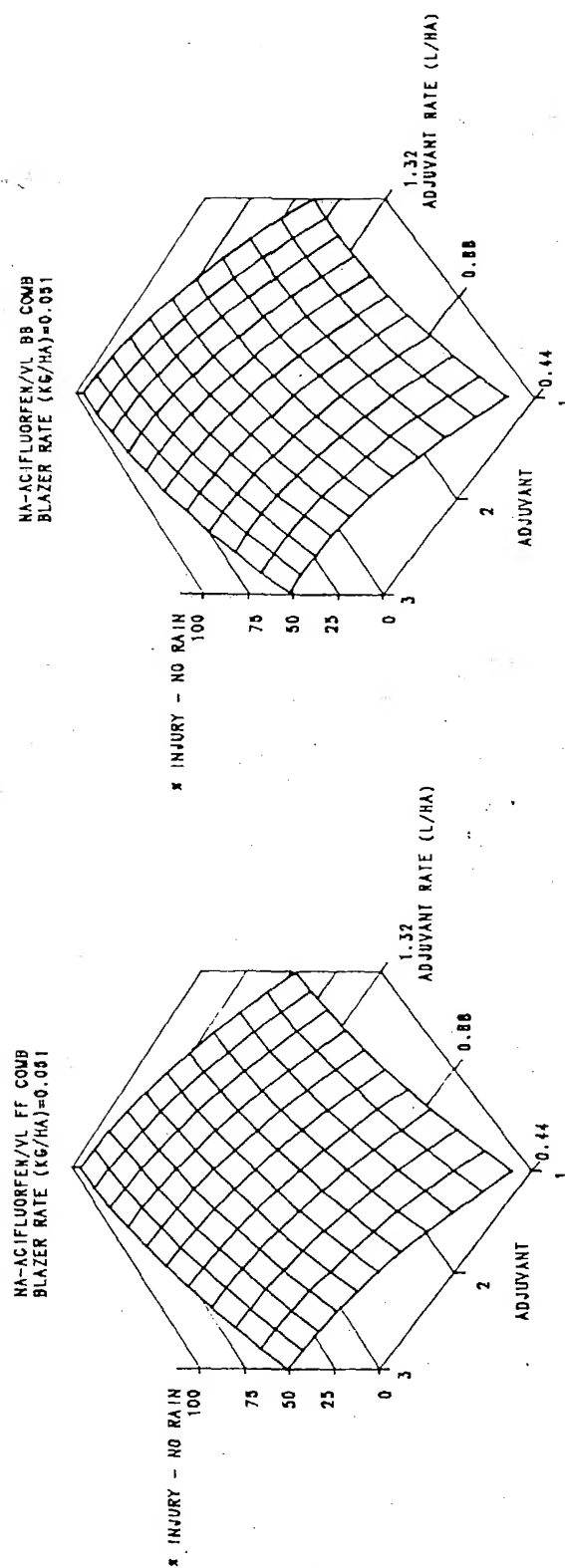


FIGURE 4. Response surfaces for factorial (left) and Box-Behnken (right) designs for the no-rain treatment with Na-acifluorfen applied at 0.051 kg/ha. Adjuvants 1, 2, and 3 correspond to adjuvants A, B, and C, respectively (see text).

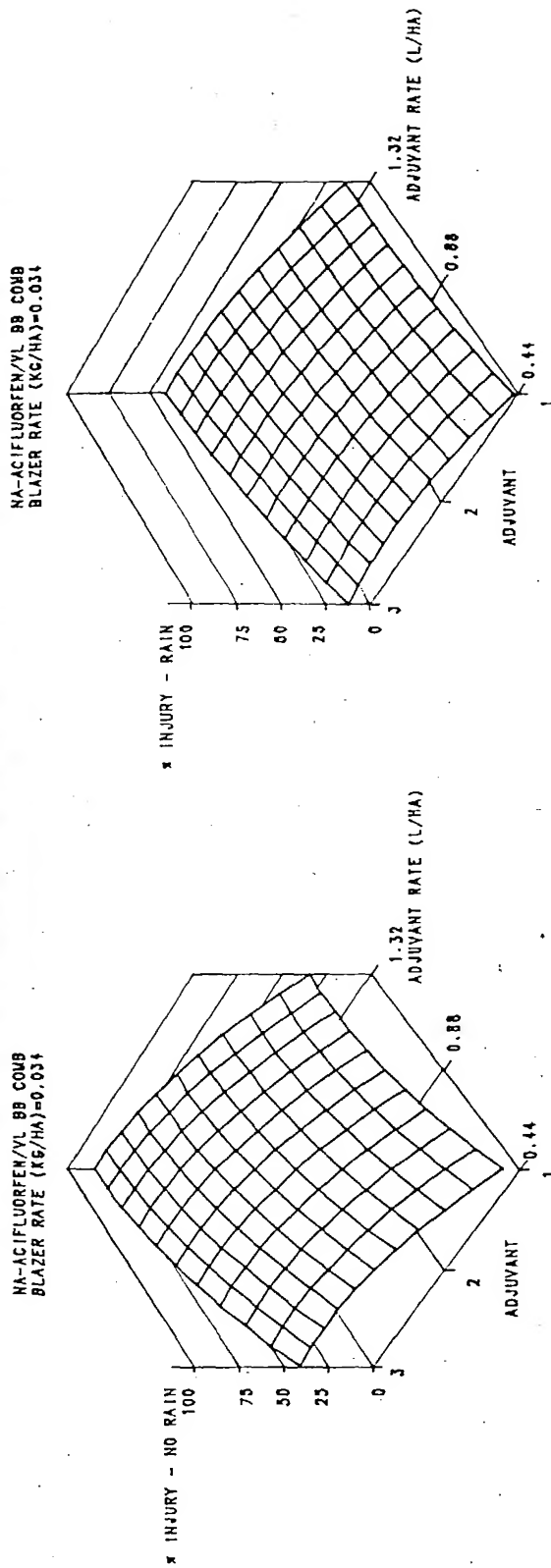


FIGURE 5. Response surfaces for the Box-Behnken design at the 0.034 kg/ha application rate of Na-acifluorfen without rain (left) and with rain (right). Adjuvants 1, 2, and 3 correspond to adjuvants A, B, and C, respectively (see text).

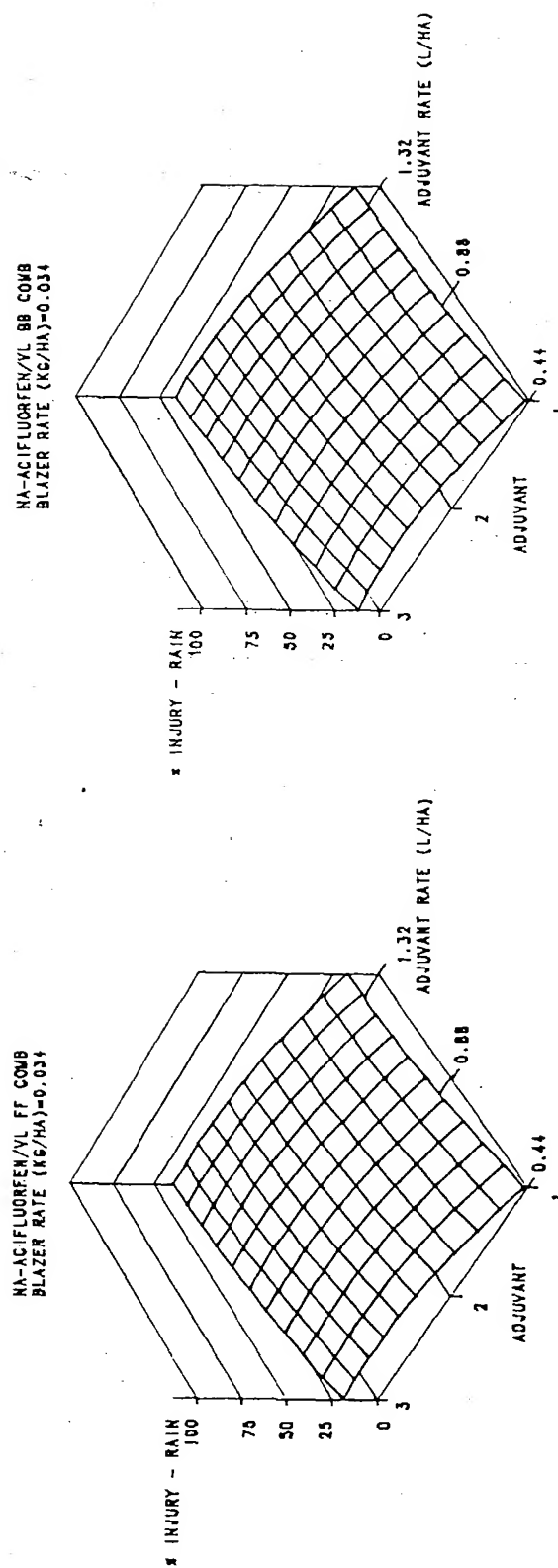


FIGURE 6. Response surfaces for the factorial (left) and Box-Behnken (right) design for the treatment receiving rainfall after the Na-acifluorefen application at 0.034 kg/ha. Adjuvants 1, 2, and 3 correspond to adjuvants A, B, and C, respectively (see text).



TABLE 4  
Comparison of  $R^2$  Correlation Values for the  
Box-Behnken and Factorial Design for  
Individual Experiments and Combined Over  
Experiments

Experiment	Box-Behnken $R^2$		Factorial $R^2$	
	No rain	Rain	No rain	Rain
1	0.9340	0.9470	0.9424	0.8812
2	0.9675	0.7982	0.9243	0.7874
Combined	0.7263	0.7227	0.9551	0.8625

the full factorial or the Box-Behnken designs are similar and appear to justify use of the time- and cost-saving Box-Behnken design for research of this nature.

In conclusion, the Box-Behnken design required only 15 treatments vs. 27 for the factorial design and yielded similar response surfaces. In a given experiment, the confidence limits were similar between the two designs. If the experiments were combined, the factorial design, with a greater number of treatments, would provide greater confidence. The adjuvant comparison of A, B, and C yielded structural information which led to the development of Dow Corning® Q2-5309 (Dow Corning Corp., Midland, MI 48686), a silicone adjuvant that increases herbicide efficacy and rainfastness even at low herbicide application rates.

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## Chapter 40

**SPECIES-SPECIFIC SENSITIVITY TO ORGANOSILICONE  
SURFACTANT-ENHANCEMENT OF GLYPHOSATE UPTAKE**

Roger J. Field, Nicole N. Dobson, and Lynnore J. Tisdall

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## ABSTRACT

The initial rate of uptake of glyphosate [*N*(phosphonomethyl)glycine] by the stomatous, adaxial surface of perennial ryegrass (*Lolium perenne* L.) was enhanced by addition of 0.1% (v/v) Silwet® L-77. Entry of solution into the leaf was initially via open stomata and associated with the low surface tension of the solution containing Silwet L-77 ( $<30 \text{ mN m}^{-1}$ ).

In other species, notably dallisgrass (*Paspalum dilatatum* Poiret.) and quackgrass (*Elytrigia repens* Beauv.), addition of Silwet L-77 did not enhance uptake of glyphosate and was usually antagonistic.

The species-specific differences were not attributed to differences in stomatal frequency or major leaf surface characteristics. The rate of droplet drying may be enhanced on planar leaf surfaces such as *P. dilatatum*, and this could be a contributing factor in the development of antagonism. Addition of 3 to 6% (v/v) glycerin as an humectant to solutions containing Silwet L-77 overcame tolerance and resulted in considerable enhancement of glyphosate uptake.

## I. INTRODUCTION

The demonstration that the organosilicone surfactant Silwet L-77 enhances herbicide uptake by promotion of stomatal infiltration of solution is of major physiological and practical significance.<sup>7,8</sup> Rapid flow of solution into the substomatal chamber necessitates formulations of low surface tension ( $<30 \text{ mN m}^{-1}$ ) and appropriate stomatal morphology.<sup>11</sup> The benefit of adding Silwet L-77 to commercial formulations of glyphosate, metsulfuron{2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoic acid}, triclopyr{[(3,5,6-trichloro-2-pyridinyl)oxy] acetic acid}, and other herbicides has been considerable in reducing the use rates of active ingredient<sup>1,3,9</sup> and is reducing the duration of the critical rainfall period.<sup>8</sup>

The early success of adding Silwet L-77 to formulated herbicides was on two species, *L. perenne*<sup>1,2</sup> and gorse (*Ulex europaeus* L.).<sup>9,14</sup> Both species possess highly ridged, stomatous leaf/spine surfaces that are covered in trichomes and platelets of epicuticular wax. The surfaces are typically difficult to wet with commercial herbicide formulations, but this is overcome by addition of 0.1 to 0.5% Silwet L-77. Addition of Silwet L-77 promotes a high rate of herbicide entry into the leaf during the initial 3 h, but final incorporation of herbicide into the leaf may not be greatly enhanced after 24 to 48 h.<sup>8</sup>

The practical use of Silwet L-77 with glyphosate formulated as Roundup® has been highly successful in overcoming seasonal tolerance of *L. perenne* to the herbicide and in the control of *U. europaeus*.<sup>1,14</sup> Unfortunately, field use of this formulation combination has revealed an uneven response by some species and some antagonism to glyphosate in others.<sup>5,6,10</sup> The objective of this chapter is to examine the physiological basis for Silwet L-77-induced antagonism of glyphosate activity in *P. dilatatum*. The experimentation focuses on the regulation of glyphosate uptake and examines the importance of both the physical attributes of herbicide solutions and leaf surfaces and the biological factors involved.

## II. MATERIALS AND METHODS

## A. PLANT MATERIAL AND GROWTH CONDITIONS

All experiments were carried out in a controlled environment chamber maintained at 20/15°C, with a photoperiod of 14 h, 70% relative humidity (RH), and a photosynthetic photon flux density (PPFD) of  $300 \mu\text{mol m}^{-2} \text{ s}^{-1}$ . Plants of *P. dilatatum* were grown in a 30/20°C temperature regime. All plants were grown in 10-cm diameter pots filled with a 1:1 medium containing a Wakanui silt loam soil and a nutrient-supplemented potting mix.

TABLE 1  
Effect of Silwet L-77 on  
Uptake of Glyphosate  
(Formulated as MON 0139) in  
*Paspalum dilatatum* after 6 h

Glyphosate formulation	Applied glyphosate absorbed (%)		
	0 <sup>b</sup>	0.1 <sup>b</sup>	0.5 <sup>b</sup>
Control <sup>a</sup>	19.5	—	—
MON 0139	19.9	17.8	9.0
SE <sup>c</sup>	—	2.48	—

<sup>a</sup> Control treatment is fully formulated glyphosate.

<sup>b</sup> Numbers refer to the % (v/v) of Silwet L-77.

<sup>c</sup> SE, standard error.

Plants of *L. perenne* (cv. Grasslands Ruanui), *P. dilatatum*, colonial bentgrass (*Agrostis tenuis* Sibth), orchardgrass (*Dactylis glomerata* L.), and Canada thistle [*Cirsium arvense* (L.) Scop.] were grown from seed, while plants of *E. repens* were propagated from 40-mm-long rhizome fragments. Plants were grown to the two- to four-leaf stage, and the youngest fully expanded leaf was used in experiments.

All experiments were fully randomized designs with a minimum of eight replicates. A minimum of 15 replicates were used in contact angle and surface tension measurements. An analysis of variance was carried out to calculate the standard errors of the means.

## B. UPTAKE METHODOLOGY

The standard application solution contained the equivalent of 0.72 kg of active ingredient (a.i.) per ha of glyphosate (as Roundup formulation) in 200 l of water per ha plus <sup>14</sup>C-glyphosate as the isopropylamine salt. The final radioactive concentration was approximately 30,000 disintegrations per minute (dpm) per microliter of solution. Adjuvants were added on a volume basis, with final concentrations of Silwet L-77 in the range of 0.1 to 0.5% (v/v) and glycerin at 3 to 6% (v/v). In the experiment described in Table 1, glyphosate was used in a surfactant-free formulation, MON 0139.

Either a single 1- $\mu$ l droplet or two 0.5- $\mu$ l droplets were applied to leaf surfaces with a microsyringe. Uptake was determined by washing the leaf surfaces with 25 ml of distilled water or a solution containing 2% glyphosate. Aliquots of the washings were mixed with Brays liquid scintillation fluid and counted. Uptake was determined by subtracting the radioactivity applied from that recovered by washing, and presented as a percentage. The duration of the uptake period was normally 6 h, except in the experiment detailed in Table 2, when it was 2 and 6 h.

In experiments where leaves were pretreated with surfactant, 0.1 to 0.5% Silwet L-77 solutions were applied with a microsprayer. The sprayer was calibrated to deliver a volume per unit area equivalent to the deposit from an application of 200 l of water per ha. Pretreatments were applied 2 or 24 h prior to the start of an uptake experiment.

## C. PHYSICAL CHARACTERISTICS OF SOLUTIONS AND LEAF SURFACES

Contact angle determinations were made by measuring the height and contact diameter of 1- $\mu$ l droplets applied to the adaxial leaf surface, and using Mack's equation.<sup>8</sup> All test



TABLE 2  
Effect of Silwet L-77 on the Uptake  
of Glyphosate in *Paspalum dilatatum*  
after 2 or 6 h

Duration of uptake (h)	Applied glyphosate absorbed (%)		
	0*	0.1*	0.5*
2	19.2	5.5	7.3
6	14.7	4.1	5.6
SE	—	3.32	—

\* Numbers refer to % (v/v) of Silwet L-77.

solutions were equivalent to those described in the previous section. The dynamic surface tension of the same solutions was determined.<sup>3,12</sup>

Sections of fully expanded leaves were taken 50 mm from the leaf tip; freeze dried, attached to aluminum stubs with double-sided adhesive tape, sputter coated with gold, and examined with a Cambridge 250 Mark 2 Scanning Electron Microscope (SEM) at 100 to 5000 magnifications. In some cases, solutions containing glyphosate and adjuvants were applied in 0.5- $\mu$ l droplets 4 to 5 h prior to freeze drying.

Chloroform treatment of leaf surfaces involved complete immersion for a fixed period, rapid aqueous washing, and visual assessment by scanning electron microscopy.

#### D. VISUALIZATION OF STOMATAL ENTRY OF SOLUTION

Sodium fluorescein (1 mg ml<sup>-1</sup>) was added to the same solutions containing glyphosate and adjuvants described above. Fifteen microliters of solution was applied to the adaxial leaf surface and removed by washing with distilled water after 1 min. The leaf surface was examined by UV microscopy within 15 min and a photographic record taken.<sup>8</sup>

### III. RESULTS

The addition of Silwet L-77 to formulations of glyphosate may enhance uptake as in *L. perenne*, may not vary uptake as in *C. arvense*, or reduce overall uptake as in *P. dilatatum* and other grass species (Table 3). The apparent antagonism of glyphosate uptake by Silwet L-77 was concentration dependent, and raising the rate from 0.1 to 0.5% (v/v) further reduced uptake. All the species tested had stomatous adaxial surfaces.

Identification of the physiological or physiochemical basis of Silwet L-77-induced antagonism of glyphosate uptake was concentrated on a study of *P. dilatatum*. The adaxial leaf surface is characterized by a stomatal density of 48 mm<sup>-2</sup>, 60% of the value for the abaxial surface. A crystalline epicuticular wax layer covers the abaxial surface and is resistant to removal following immersion in chloroform for 2 to 5 s. A 10-s immersion removed approximately 50% of the crystalline wax. In contrast a 2-s chloroform treatment removed virtually all the crystalline wax from the abaxial leaf surface. Trichomes were found on both surfaces, although predominantly the abaxial.

The pattern of response of *P. dilatatum* to the addition of Silwet L-77 was established within 2 h, with a 71.4 and 78.6% reduction in glyphosate uptake after addition of 0.1 and 0.5% Silwet L-77 respectively (Table 2). The greater antagonism of glyphosate uptake following addition of the higher rate of Silwet L-77 was not linked to major changes in



TABLE 3  
Effect of Silwet® L-77 on Uptake of  
Glyphosate by Several Species after 6 h

Species	Applied glyphosate absorbed (%)			SE
	0*	0.1*	0.5*	
<i>Agrostis tenuis</i>	26.8	8.0	—	2.54
<i>Cirsium arvense</i>	14.3	16.4	—	2.16
<i>Dactylis glomerata</i>	21.1	12.8	7.3	2.01
<i>Elytrigia repens</i>	46.8	27.9	22.6	4.74
<i>Lolium perenne</i>	12.8	28.1	—	3.74
<i>Paspalum dilatatum</i>	17.0	6.4	4.8	2.35

\* Numbers refer to % (v/v) of Silwet-77.

TABLE 4  
Effect of Including Silwet L-77 and/or Glycerin with  
Formulated Glyphosate on Surface Tension and Contact  
Angle with the Adaxial Surface of a *Paspalum dilatatum*  
Leaf

Silwet L-77 (%)		Glycerin (%)		Surface tension (mN m <sup>-1</sup> )	Contact angle (°)	Time for complete wetting (s)
0	0.1	0	6			
x		x		45.7 (0.03)	88.0 (9.29)	NW
	x	x		24.1 (0.01)	0	19
x			x	44.3 (0.04)	100.2 (5.23)	NW
	x		x	25.6 (0.08)	45.0 (8.90)	120—180

Note: Standard error of mean given in parentheses. NW denotes no complete wetting by droplet.

From Tisdall, L. J., Mechanism of Silwet L-77 — reduced antagonism of glyphosate efficacy on *Paspalum dilatatum*, Dissertation, Lincoln University, Canterbury, New Zealand.

solution surface tension or droplet contact angles with the leaf surface. The inclusion of 0.1% Silwet L-77 in solutions of formulated glyphosate reduced surface tension from 45.7 to 24.1 mN m<sup>-1</sup> (Table 4), with further increases in Silwet L-77 concentration to 0.5% giving a minimal reduction in surface tension of less than 5%. The contact angle of control solutions was 88°, with addition of 0.1 to 0.5% Silwet L-77 giving a nonmeasurable contact angle and complete surface wetting within 5 s.

Pretreating adaxial leaf surfaces with 0.1 to 0.5% Silwet L-77 enhanced the uptake of subsequently applied glyphosate (Table 5). A 2-h pretreatment with 0.5% Silwet L-77, which had dried by the time of glyphosate application, resulted in a threefold increase in glyphosate uptake. In a further experiment, it was shown that addition of Silwet L-77 to glyphosate did not enhance glyphosate uptake even when adaxial leaf surfaces had been pretreated with 0.5% Silwet L-77 for 24 h (Table 6).

The results suggest a complex interaction between formulated glyphosate, Silwet L-77, and the plant surface. Scanning electron microscopy of adaxial surfaces revealed no damage associated with the application of 0.1 to 0.5% Silwet L-77 solutions up to 24 h prior to tissue preparation.

TABLE 5  
Effect of Silwet L-77  
Pretreatment on the Uptake  
of Glyphosate in  
*Paspalum dilatatum*  
after 6 h

Duration (h)	Applied glyphosate absorbed (%)		
	0*	0.1*	0.5*
2	8.1	11.5	24.1
24	7.4	8.4	17.1
SE	—	3.50	—

\* Numbers refer to % (v/v) of Silwet L-77 pretreatment.

TABLE 6  
Effect of Silwet L-77  
Pretreatment for 24 h on the  
Uptake of Glyphosate in  
*Paspalum dilatatum* after 6 h

Silwet L-77 (%) pretreatment	Applied glyphosate absorbed (%)		
	0*	0.1*	0.5*
0	9.8	9.5	4.1
0.5	16.3	7.2	9.1
SE	—	3.25	—

\* Numbers refer to % (v/v) of Silwet L-77 pretreatment.

The possibility of an undesirable interaction between Silwet L-77 and MON 0818, the surfactant in formulated glyphosate, was tested by use of the surfactant-free formulation of glyphosate, MON 0139. Addition of Silwet L-77 to MON 0139 caused antagonism of glyphosate uptake, particularly at the 0.5% use rate (Table 1).

The antagonism of glyphosate uptake by Silwet L-77 was overcome, and uptake positively promoted, by addition of the humectant, glycerin (Table 7). Glycerin per se had no influence on the uptake of glyphosate, but in the presence of Silwet L-77, there was significant enhancement of uptake. The response was concentration related, with 6% glycerin increasing glyphosate uptake from 14.4 to 34.3% in the presence of 0.1% Silwet L-77. Addition of 6% glycerin only increased the surface tension of application solutions marginally (24.1 to 25.6 mN m<sup>-1</sup>), but did extend the time for complete droplet wetting, enabling an initial contact angle of 45° to be measured (Table 4). Improved uptake was not attributed to leaf surface damage, as determined by scanning electron microscopy.

Washing the adaxial surface of *P. dilatatum* 1 min after application of glyphosate solutions containing sodium fluorescein revealed no fluorescence associated with stomata. Addition of 0.1% Silwet L-77 produced fluorescence of stomata and areas beneath the cuticle equivalent to approximately three stomatal diameters.

TABLE 7  
The Effect of Silwet L-77 and Glycerin  
on the Uptake of Glyphosate in  
*Paspalum dilatatum* after 6 h

Silwet L-77 (%)		Glycerin (%)			Applied glyphosate absorbed (%)
0	0.1	0	3	6	
x		x			14.5
	x	x			14.4
x			x		12.6
x				x	11.0
	x		x		25.0
	x			x	34.3
SE					3.46

#### IV. DISCUSSION

The addition of Silwet L-77 to formulations containing glyphosate may result in substantial increases in foliar uptake of the herbicide (Table 3).<sup>8</sup> The responses of *L. perenne*<sup>1</sup> and *U. europaeus*<sup>14</sup> are the most notable, and the rapidity of herbicide uptake has been attributed to rapid stomatal infiltration by solution. The assertions that low solution surface tension ( $<30 \text{ mN m}^{-1}$ ) is necessary for stomatal infiltration, provided certain physical requirements of wall angles in the stomatal pore are met,<sup>11</sup> have been confirmed by recent experiments with Silwet L-77.<sup>8</sup>

The reason for the observed antagonism in *P. dilatatum* does not reside in simple leaf morphology differences or in the response of the adaxial leaf surface to solutions containing Silwet L-77. The adaxial surface is stomatous and the frequency is similar to *L. perenne*.<sup>5</sup> Droplets containing 0.1% Silwet L-77, or higher rates, were rapidly spread, with complete wetting occurring within 19 s (Table 4). While the adaxial leaf surface of *P. dilatatum* is less ridged than that of *L. perenne*,<sup>2,8</sup> it is not smooth and has regularly arranged platelets of epicuticular wax. The resistance of the wax platelets to chloroform suggests that its composition, although not necessarily its physical characteristics, vary from that of *L. perenne*.<sup>5</sup> The presence of fluorescence around stomata in formulations containing Silwet L-77 can be interpreted as indicating some stomatal infiltration of solution.<sup>8</sup> This observation is consistent with the known mode of action of Silwet L-77, and low levels of fluorescence are reasonably interpreted as indicating limited stomatal entry of solution. This is consistent with the limited uptake of glyphosate that occurred in the presence of Silwet L-77 (Tables 2 and 3). At this stage, it is reasonable to conclude that at least a portion of glyphosate uptake with Silwet L-77 is stomatal, while in the absence of the surfactant, uptake is by a cuticular pathway. The fluorescence investigations do not explain why stomatal uptake is apparently short term and clearly at variance with results obtained for *L. perenne*.<sup>7,8</sup>

The lack of leaf surface damage associated with the addition of Silwet L-77 and the observed slow increase in uptake over time (Table 2) suggest that the surfactant was not grossly interfering with the uptake pathway. The suggestion that 0.5% Silwet L-77 was perhaps less effective in promoting glyphosate uptake than 0.1% (Table 2) is contrary to the pattern of short-term uptake in *L. perenne*<sup>8</sup> and other species.<sup>14</sup>

The sequential application of Silwet L-77 followed by formulated glyphosate (Table 5) permitted rapid droplet spreading without antagonism of uptake. That the sequential application of Silwet L-77 and glyphosate enhanced herbicide uptake (Table 5), while pretreatment

with Silwet L-77 followed by application of glyphosate plus Silwet L-77 did not (Table 6), suggests that antagonism is related to the interaction of Silwet L-77 with components in the formulated glyphosate. Such an interaction would have to involve the specific response of leaf surfaces of species shown to be antagonistic. Elimination of MON 0818, the surfactant in formulated glyphosate, did improve uptake at 0.1% Silwet L-77, but with no major change at the higher rate (Table 1). The results were equivocal, but suggested that antagonism may involve MON 0818 and its interaction with Silwet L-77 on specific leaf surfaces. The finding that the presence of MON 0818 confers no advantage to glyphosate uptake in the absence of Silwet L-77 is contradictory to other findings.<sup>13</sup>

One approach to resolving the antagonism problem was to design a formulation that had slightly different physical properties, but that retained the potential advantage of containing Silwet L-77. The virtually instantaneous complete wetting of solutions containing Silwet L-77 suggests rapid drying of deposits and some adverse effects on uptake. In *L. perenne*, the initial rate of uptake by the stomatal pathway was  $16.5\% \text{ h}^{-1}$  during the first hour after application, falling to  $9.0\% \text{ h}^{-1}$  between 2 and 3 h after application.<sup>8</sup> Stomatal infiltration was reduced during the latter period, and other pathways dominated. The rate of drying of deposits on *L. perenne* is probably slower than on *P. dilatatum*, owing to the semiprotected compartments between the ridges on the leaf surface and perhaps because of the greater presence of trichomes. There is evidence that even on plain wax surfaces, the rate of drying of deposits containing Silwet L-77 is more rapid than in the absence of the adjuvant.<sup>9</sup>

The addition of the humectant glycerin overcame the antagonism induced by Silwet L-77, while not conferring any advantage when used in the absence of the surfactant (Table 7).<sup>4</sup> Glycerin slowed the drying of deposits, but it seems unlikely that its positive effect was simply related to this physical phenomenon.

The role of humectants in the herbicide uptake process is poorly described in the literature. The addition of glycerin had some limited effects on the surface tension of solutions and their leaf wetting characteristics (Table 4). Perhaps importantly, these changes did not contravene the physical parameters previously established for stomatal entry of solution.<sup>11</sup> Given this information and the lack of evidence to support Silwet L-77-induced effects on stomatal response, it is necessary to verify the hypothesis that rapid drying of herbicide deposits is a contributory factor in antagonism.

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## Chapter 41

**INFLUENCE OF A MINERAL OIL ADJUVANT ON THE  
ANTAGONISM OF SETHOXYDIM, CYCLOXYDIM, AND  
CLETHODIM BY BENTAZON**

Per Kudsk, S. Kopp Mathiasen, and Torben Olesen

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## ABSTRACT

The influence of a mineral oil on the antagonistic effect of bentazon [(3-(1-methylethyl)-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide)] on the phytotoxicity of the graminicides sethoxydim {(2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one)}, cycloxydim {(2-[1-(ethoxyimino)butyl]-3-hydroxy-5-(3-thiamyl)-2-cyclohexen-1-one)}, and clethodim {((*E,E*)- $\pm$ -2-[1-[[3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one)} was examined on pot-grown barley (*Hordeum vulgare* L. cv. Igri). The results were analyzed using a parallel-line assay technique.

It was found that bentazon significantly reduced the activity of all three cyclohexadiones. Addition of a mineral oil adjuvant significantly increased the herbicidal effect of the graminicides whether bentazon was added or not. While the mineral oil reduced the severity of the antagonistic effect of bentazon on sethoxydim increasingly with increasing concentration of the adjuvant, no reduction in antagonism was found on cycloxydim and clethodim. Applying the parallel-line assay technique, it was possible to determine that the reduced antagonistic effect of bentazon on sethoxydim phytotoxicity, when adding the mineral oil, was caused by a reduced interaction between the two herbicides, and not merely the result of the increased phytotoxicity of the graminicide.

## I. INTRODUCTION

In order to control the whole spectrum of weed species present in a crop, it is often necessary to tank mix two or more herbicides. An example is tank mixtures of selective graminicides controlling grass weeds and other herbicides controlling broadleaved weeds. One group of selective graminicides is the cyclohexadiones; however, it has been found that the phytotoxicity of sethoxydim is reduced when applied in tank mixture with, e.g., bentazon.<sup>2,7,11</sup> Rhodes and Coble<sup>13</sup> found that bentazon reduced the uptake of <sup>14</sup>C-sethoxydim into leaves of goosegrass [*Eleusine indica* (L.)] and that the difference in uptake could account for the antagonistic effect of bentazon on sethoxydim phytotoxicity. Retzlaff et al.<sup>12</sup> and Kobek et al.,<sup>9</sup> using leaf segments, isolated intact chloroplasts and a crude enzyme preparation from isolated chloroplasts, found that the antagonistic effect of bentazon on sethoxydim and cycloxydim occurred at the membrane level.

Adjuvants can increase foliar uptake and change membrane permeability,<sup>6</sup> and it seems feasible that adjuvants may affect interactions among herbicides. The objective of this study was to assess the influence of various doses of a mineral oil on the antagonistic effect of bentazon on the phytotoxicity of three cyclohexadione herbicides: sethoxydim, cycloxydim, and clethodim. Another objective was to illustrate how a parallel-line assay technique can be applied to assess interactions between herbicides when one of the herbicides can be considered herbicidally inactive on the test plant.

## II. MATERIALS AND METHODS

### A. PLANT CULTURE

Three experiments were conducted in a greenhouse, one with each of the selective graminicides sethoxydim, cycloxydim, and clethodim. Twenty plants of barley were grown in 8-l pots in a soil-peat mixture (30:70%, vol.) containing all necessary macro- and micronutrients. The pots were subirrigated automatically several times daily.

## B. TREATMENT OF PLANTS

Four doses of sethoxydim and cycloxydim and five doses of clethodim were applied at the four- to five-leaf stage. The graminicides were applied either alone or in a tank mixtures with 960 g ha<sup>-1</sup> bentazon. Both the graminicides alone and the tank mixtures with bentazon were applied without additional adjuvant or with 0.5, 2, or 8 l ha<sup>-1</sup> Actipron®, a mineral oil adjuvant consisting of 97% mineral oil and 3% emulsifier. The herbicides were applied with a laboratory pot sprayer fitted with one Hardi 4110-16 flat fan nozzle operated at a pressure of 300 kPa and delivering a volume rate of 200 l ha<sup>-1</sup>. All herbicides were applied as their commercial formulations. The barley plants were harvested 3 weeks after herbicide application, and the fresh and dry weights recorded. Because of similar results in the statistical analyses, only the dry weight results are presented.

## C. STATISTICS

Bentazon and the mineral oil are only expected to affect the amount of active ingredient reaching the site of action by influencing the penetration into the leaf, whereas the mode of action of the graminicides can be assumed not to be affected. Further, as neither bentazon nor the adjuvant is expected to affect the growth of the barley plants when applied separately, the dose-response curves of the graminicides applied alone and in tank mixtures can be assumed to be parallel. Accordingly, the results can be analyzed by applying a parallel-line assay technique.<sup>5</sup>

A Box-Cox<sup>1</sup> power transformation indicated that in all three experiments a log transformation minimized the residual sum of squares and, consequently, the following nonlinear five-parameter regression model, expressing dry weight ( $U$ ) as a function of herbicide dose ( $z$ ),

$$\log_e(U_i) = \log_e\{(D - C)/[1 + \exp(-2(a + b \log_{10}(R_i z)))] + C\} + e \quad (1)$$

was fitted simultaneously to the eight dose-response curves within each experiment ( $i = 1$  to 8). The parameters  $D$  and  $C$  denote the upper and lower limits at zero dose and large doses, respectively,  $a$  describes the horizontal location, and  $b$  is proportional to the slope around  $ED_{50}$ , while  $R_i$  is the relative potency of the graminicides applied in the tank mixture with bentazon and/or mineral oil compared to the graminicide applied alone. The relative potency expresses the ratio of the herbicide doses giving similar effects.

The concept of the parallel-line assay and its application in herbicide studies has been discussed in more detail elsewhere.<sup>10,14</sup>

In all experiments, bentazon and the three doses of the mineral oil were included separately and in combination to test whether the growth of the barley plants was affected. The regressions were evaluated by a test for lack of fit and graphical analyses of residuals.<sup>4</sup>

## III. RESULTS AND DISCUSSION

Bentazon or the mineral oil applied separately or together had no significant effect on the growth of the barley plants in any of the three experiments, and could therefore be considered biologically inert.

The estimated parameters and relative potencies from the sethoxydim, cycloxydim, and clethodim experiments, are shown in Tables 1 to 3, respectively. Addition of 960 g ha<sup>-1</sup> bentazon significantly reduced the phytotoxicity of all three graminicides; however, sethoxydim was antagonized more by bentazon ( $R = 0.40$ ) than cycloxydim ( $R = 0.60$ ) and clethodim ( $R = 0.73$ ). Relative potencies of 0.40, 0.60, and 0.73 show that it was necessary to increase the dose of sethoxydim, cycloxydim, and clethodim 2.5, 1.7, and 1.4 times, respectively, to maintain the effect on barley when bentazon was added.

TABLE 1  
Estimated Parameters and Relative Potencies of  
Sethoxydim

<i>D</i> (g per pot)	<i>C</i> (g per pot)	<i>a</i>	<i>b</i>
22.02 (20.96–23.09)	3.90 (3.61–4.20)	9.04 (7.60–10.48)	–4.22 (–4.86 to –3.59)
Treatment	Relative potency	ED <sub>50</sub> (g ha <sup>–1</sup> )	
Sethoxydim alone	1.00	138.7	
+ 0.5 l ha <sup>–1</sup> mineral oil	1.43 (1.27–1.59)	97.0	
+ 2.0 l ha <sup>–1</sup> mineral oil	1.70 (1.52–1.89)	81.6	
+ 8.0 l ha <sup>–1</sup> mineral oil	2.80 (2.48–3.11)	49.5	
Sethoxydim + 960 g ha <sup>–1</sup> bentazon	0.40 (0.35–0.44)	346.8	
+ 0.5 l ha <sup>–1</sup> mineral oil	0.89 (0.80–0.99)	155.9	
+ 2.0 l ha <sup>–1</sup> mineral oil	1.46 (1.30–1.63)	95.0	
+ 8.0 l ha <sup>–1</sup> mineral oil	2.45 (2.18–2.73)	56.6	

Note: Figures in parentheses are approximate 95% confidence intervals.

*D*, upper limit; *C*, lower limit; *a*, horizontal location; *b* proportional to slope around ED<sub>50</sub>.

TABLE 2  
Estimated Parameters and Relative Potencies of  
Cycloxydim

<i>D</i> (g per pot)	<i>C</i> (g per pot)	<i>a</i>	<i>b</i>
57.22 (53.80–60.63)	10.97 (10.37–11.57)	11.94 (9.61–14.27)	– 6.12 (– 7.27 to – 4.97)
Treatment	Relative potency	ED <sub>50</sub> (g ha <sup>-1</sup> )	
Cycloxydim	1.00	89.3	
+ 0.5 l ha <sup>-1</sup> mineral oil	3.23 (2.83–3.64)	27.7	
+ 2.0 l ha <sup>-1</sup> mineral oil	3.63 (3.22–4.04)	24.6	
+ 8.0 l ha <sup>-1</sup> mineral oil	5.43 (4.72–6.15)	16.5	
Cycloxydim + 960 g ha <sup>-1</sup> bentazon	0.60 (0.53–0.67)	148.9	
+ 0.5 l ha <sup>-1</sup> mineral oil	1.43 (1.25–1.62)	62.5	
+ 2.0 l ha <sup>-1</sup> mineral oil	1.74 (1.53–1.94)	51.3	
+ 8.0 l ha <sup>-1</sup> mineral oil	2.58 (2.27–2.90)	34.6	

Note: Figures in parentheses are approximate 95% confidence intervals.

*D*, upper limit; *C*, lower limit; *a*, horizontal location; *b* proportional to slope around ED<sub>50</sub>.



TABLE 3  
Estimated Parameters and Relative Potencies of  
Clethodim

<i>D</i> (g per pot)	<i>C</i> (g per pot)	<i>a</i>	<i>b</i>
58.23 (53.80-62.66)	12.89 (12.06-13.73)	3.75 (2.98-4.53)	-2.83 (-3.33 to -2.34)
Treatment	Relative potency	ED <sub>50</sub> (g ha <sup>-1</sup> )	
Clethodim	1.00	21.1	
+ 0.5 l ha <sup>-1</sup> mineral oil	2.03 (1.67-2.40)	10.4	
+ 2.0 l ha <sup>-1</sup> mineral oil	2.93 (2.40-3.46)	7.2	
+ 8.0 l ha <sup>-1</sup> mineral oil	4.94 (4.05-5.84)	4.3	
Clethodim + 960 g ha <sup>-1</sup> bentazon	0.73 (0.60-0.86)	29.0	
+ 0.5 l ha <sup>-1</sup> mineral oil	1.37 (1.12-1.62)	15.4	
+ 2.0 l ha <sup>-1</sup> mineral oil	2.09 (1.71-2.47)	10.1	
+ 8.0 l ha <sup>-1</sup> mineral oil	2.91 (2.38-3.44)	7.3	

Note: Figures in parentheses are approximate 95% confidence intervals.

*D*, upper limit; *C*, lower limit; *a*, horizontal location; *b* proportional to slope around ED<sub>50</sub>.

In a preliminary study, it was found that the antagonistic effect of bentazon on sethoxydim was promoted when the dose of bentazon was increased from 480 to 1440 g ha<sup>-1</sup>, indicating that the molar ratio between sethoxydim and bentazon in the spray solution influenced the antagonism (data not shown). However, the different response to bentazon of the cyclohexanedione herbicides examined in this experiment cannot be explained on a molar ratio basis. The molecular weights of the three graminicides are almost identical, and as cycloxydim and sethoxydim, due to their higher activity on barley as illustrated by the ED<sub>50</sub> values in Tables 1 to 3, were applied at lower doses than sethoxydim, the molar ratio between the graminicide and bentazon was actually lower in the cycloxydim and clethodim spray solutions.

The phytotoxicity of cycloxydim and clethodim was generally increased more by the mineral oil than was that of sethoxydim. However, the activity of all three graminicides was enhanced significantly when the mineral oil was added, and increasing the dose of the adjuvant from 0.5 to 2 and from 2 to 8 l ha<sup>-1</sup> increased the phytotoxicity of the graminicides whether bentazon was included in the spray solution or not.

In order to examine whether the mineral oil had any influence on the antagonistic effect of bentazon on the graminicides, it is necessary to compare the effect of the tank mixtures with bentazon with the effect of the corresponding tank mixtures without bentazon. The results from Tables 1 to 3 are summarized in Table 4 by expressing the potencies of the corresponding treatments without bentazon. The increase in the relative potency of sethoxydim found with an increasing amount of mineral oil in the tank mixture of sethoxydim and bentazon shows that the mineral oil reduced the severity of the antagonism. Increasing the dose of the mineral oil beyond 2 l ha<sup>-1</sup> did not significantly influence the interaction between the two herbicides. It should be noted, however, that even when adding 8 l ha<sup>-1</sup> of mineral oil, the relative potency was significantly different from 1.0, indicating that the mineral oil reduced, but did not eliminate, the antagonistic effect of bentazon on sethoxydim phytotoxicity.



TABLE 4  
Influence of a Mineral Oil on the Relative Potency of  
Sethoxydim, Cycloxydim, and Clethodim in Tank Mixture with  
960 g ha<sup>-1</sup> Bentazon vs. the Corresponding Treatment without  
Bentazon

Treatment	Sethoxydim	Cycloxydim	Clethodim
No adjuvant	0.40(0.35-0.44)	0.60(0.53-0.67)	0.73(0.59-0.86)
0.5 l ha <sup>-1</sup> mineral oil	0.62(0.56-0.69)	0.44(0.39-0.50)	0.67(0.55-0.80)
2.0 l ha <sup>-1</sup> mineral oil	0.86(0.76-0.96)	0.48(0.42-0.53)	0.71(0.58-0.84)
8.0 l ha <sup>-1</sup> mineral oil	0.88(0.78-0.98)	0.48(0.42-0.53)	0.59(0.48-0.70)

Note: Figures in parentheses are 95% confidence intervals.

The sethoxydim results were confirmed in further experiments, as 960 g bentazon ha<sup>-1</sup> reduced the relative potency of the graminicide applied without additional adjuvant to 0.37 on barley and 0.23 on italian ryegrass (*Lolium multiflorum*), while relative potencies of 0.66 and 0.51, respectively, were found when 2 l ha<sup>-1</sup> of the mineral oil was included in the spray solution. The experiments with and without adjuvant were not conducted simultaneously, as in the present study, however, the variation in the relative potencies between experiments has been found to be insignificant, and it therefore seems unlikely that the differences observed with and without adjuvant can be attributed to differences in environment or other variable factors.

With cycloxydim and clethodim, different responses to the presence of the mineral oil were observed. Addition of the adjuvant increased the antagonistic effect of bentazon on cycloxydim phytotoxicity irrespective of the dose of the mineral oil, while the mineral oil did not significantly influence the interaction between clethodim and bentazon (Table 4). Rhodes and Coble<sup>13</sup> were unable to find any clear effect of a mineral concentrate on the antagonistic effect of bentazon on sethoxydim phytotoxicity on three grass weeds. This discrepancy could have been caused by the use of different adjuvants and/or plant species. There seem to be no reports concerning the influence of adjuvants on the interaction of bentazon on cycloxydim and clethodim phytotoxicity; however, Keeney et al.<sup>8</sup> found that a mineral oil concentrate reduced the antagonistic effect of bentazon on the uptake of the methyl ester of <sup>14</sup>C-haloxyfop (2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid), a selective graminicide belonging to the group of polycyclic alkanolic acids which have also been found to be antagonized by bentazon.<sup>3</sup>

The different effects of the mineral oil on the interaction between bentazon and the graminicides are shown graphically in Figures 1a to 1c. The three figures illustrate that while the adjuvant reduced the horizontal distance between the sethoxydim and sethoxydim plus bentazon dose-response curves (a), the distance increased between the corresponding cycloxydim dose-response curves (b), and no effect was found on the distance between the clethodim dose-response curves (c).

In practice, addition of a mineral oil is recommended when applying the graminicides and, hence, addition of 2 l ha<sup>-1</sup> mineral oil to the spray solution can be regarded as the standard treatment. The different responses of the three graminicides to addition of the adjuvant implies that while it was possible to significantly increase the phytotoxicity of sethoxydim and maintain the phytotoxicity of clethodim in tank mixture with bentazon by increasing the dose of the mineral oil to 8 l ha<sup>-1</sup> (Tables 1 and 3), bentazon significantly reduced the herbicidal activity of cycloxydim compared to the standard treatment, irrespective of the dose of the adjuvant (Table 2).

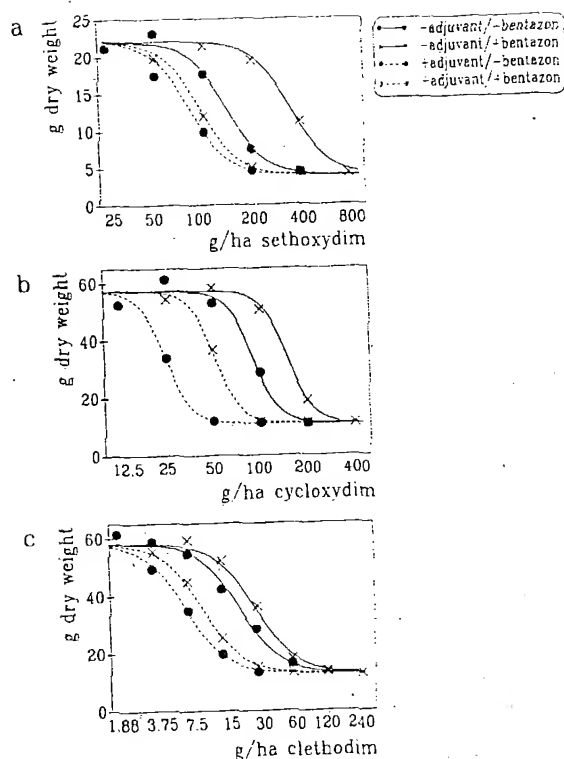


FIGURE 1. Influence of  $2 \text{ l ha}^{-1}$  mineral oil on the antagonistic effect of  $960 \text{ g ha}^{-1}$  bentazon on the phytotoxicity of (a) sethoxydim, (b) cycloxydim, and (c) clethodim. The curves and markers are the estimated dose-response curves and recorded dry weights, respectively.

The variable response of the three graminicides to the effect of the mineral oil on the antagonism by bentazon, as well as the general difference in the severity of the antagonism, probably is caused by differences in the physicochemical properties of either the active ingredients per se or the formulations.

This study has shown that adjuvants may overcome interactions between herbicides otherwise leading to a reduced phytotoxicity. Further, the study has shown that the parallel-line assay can be used to study interactions between herbicides when only one is herbicidally active on the examined plant species. As illustrated, one of the advantages of applying this technique is that it was possible to quantify more precisely the influence of bentazon on the phytotoxicity of the graminicides and, consequently, to recommend how much the dose of the graminicide or the adjuvant had to be increased to obtain the same level of control in tank mixture with bentazon vs. application of the graminicide alone.

Addition of an adjuvant often increases the effect of a herbicide. On the basis of the results of one or two doses, it is therefore difficult to determine whether a reduction in the severity of the antagonism caused by an adjuvant is merely the result of the generally increased effect level masking any interaction between the two herbicides or is caused by a direct effect of the adjuvant on the interaction between the two herbicides. This problem can be overcome by applying a parallel-line assay technique, as illustrated in this study. A comparison of Tables 1 to 3 with Table 4 shows that it is possible to distinguish between the effect of the adjuvant on the activity of the graminicide and on the antagonism by bentazon.

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## Chapter 42

THE EFFECT OF ADJUVANTS ON THE RAINFASTNESS OF  
THIFENSULFURON AND TRIBENURON

Per Kudsk

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## ABSTRACT

The rainfastness of thifensulfuron {3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid} and tribenuron {2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoic acid} was examined in four pot experiments. The herbicides were applied alone or in a tank mixture with 0.1% (v/v) nonionic surfactant, 1% (v/v) vegetable oil, 1% (v/v) mineral oil concentrate, 2.5% (w/v) ammonium sulfate, 0.025% (v/v) organosilicone surfactant, and 0.5% (v/v) cationic surfactant or 0.15% (v/v) of a synthetic latex. Three mm of rain was applied 2 and 4 h after herbicide application using a rain simulator. The results were analyzed using a parallel-line assay technique.

The phytotoxicity of both herbicides applied alone was reduced significantly by rain 2 and 4 h after spraying. All adjuvants except ammonium sulfate improved the rainfastness of thifensulfuron. Full rainfastness was obtained 2 h after application in a tank mixture with the vegetable oil or the synthetic latex. Only ammonium sulfate and the cationic surfactant did not improve the rainfastness of tribenuron, while the vegetable oil and the organosilicone surfactant gave full rainfastness 2 h after herbicide application.

## I. INTRODUCTION

Although the sulfonylurea herbicides are a relatively new class of herbicides, they are already widely used. All the sulfonylurea herbicides are both foliar and soil active, and as the first-developed compounds are relatively persistent, soil activity probably makes up an important part of their overall effect in the field, at least under more humid conditions. However, a new group of short-residual sulfonylurea herbicides have been developed, the first two compounds being thifensulfuron and tribenuron. Under normal soil conditions, these herbicides are degraded very rapidly, and when used postemergence, as recommended, the foliar activity can be considered to be more important than the soil activity. Consequently, it can be anticipated that the phytotoxicity of these herbicides will be more adversely affected by rain shortly after application than, e.g., chlorsulfuron {2-chloro-*N*-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzene sulfonamide} and metsulfuron {2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoic acid}.

In a previous study, we found that none of the sulfonylurea herbicides could be considered very rainfast, as rain 4.5 h after herbicide application significantly reduced the phytotoxicity of chlorsulfuron, metsulfuron, CGA-131036 (*N*-(6-methoxy-4-methyl-1,3,5-triazin-2-ylaminocarbonyl)-2-(2-chloroethoxy)-benzenesulfonamide), thifensulfuron, and tribenuron.<sup>8</sup> However, addition of 0.1% (v/v) of a nonionic surfactant (nonylphenol polyoxyethylene) significantly increased the rainfastness of all five herbicides.

The objective of this study was to extend the results from the previous study and examine the influence of various adjuvants on the rainfastness of the two short-residual sulfonylurea herbicides, thifensulfuron, and tribenuron.

## II. MATERIALS AND METHODS

### A. PLANT CULTURE

Four experiments, two with each of the herbicides thifensulfuron and tribenuron, were conducted using white mustard [*Sinapis alba* (L.) cv. Bixley] as a test plant. The plants were grown in a greenhouse in 8-l pots in a soil-peat mixture containing all necessary macro- and micronutrients. The pots were subirrigated automatically several times daily. Prior to herbicide application, the number of plants was reduced to six per pot.



## B. TREATMENT OF PLANTS

Four doses of thifensulfuron and tribenuron, both in the form of the methyl ester, were applied at the two-leaf stage at a volume rate of 190 l ha<sup>-1</sup> using a laboratory pot sprayer fitted with two Hardi 4110-14 flat fan nozzles operated at a pressure of 300 kPa. In the first experiment with each herbicide, the sulfonylurea herbicide was applied either alone or in a tank mixture with 0.1% (v/v) of the nonionic surfactant Lissapol® (nonylphenol polyoxyethylene), 1% (v/v) of the vegetable oil Codacide® (95% rapeseed oil with 5% emulsifier), 1% (v/v) of the mineral oil concentrate Aplus 411F (85% mineral oil with 15% emulsifier), or 2.5% (w/v) ammonium sulfate. In the second experiment, the herbicides were applied alone or in a tank mixture with 1% (v/v) Codacide, 0.025% (v/v) of the organosilicone surfactant Silwet® L-77, and 0.5% (v/v) of the fatty amine ethoxylate Frigate® or 0.15% (v/v) of the synthetic latex Spraymate Bond (45% synthetic latex with 10% emulsifier). The herbicides were applied as their commercial formulations. Three millimeters of rain at an intensity of 9 mm h<sup>-1</sup>, was applied to groups of plants 2 and 4 h after herbicide application using a rain simulator, as previously described by Kristensen.<sup>6</sup> The plants were harvested 3 weeks after spraying, and the fresh and dry weights were recorded. As the statistical analyses of the fresh and dry weights gave similar results, only the results from the analyses on the fresh weights are shown.

## C. STATISTICS

If an adjuvant increases the efficacy of a herbicide, it is often difficult to assess the influence of the adjuvant on the rainfastness of the herbicide, as it is difficult to determine whether an improved performance, in the event that rain occurs shortly after application, is merely due to the generally increased effect level or to a better rainfastness of the spray deposit. One way to overcome this problem is, in a preliminary experiment, to determine the dose-response curves of the herbicide with and without the adjuvant and then, in the subsequent experiment, apply doses inducing equivalent levels of phytotoxicity, as was done by Behrens and Elakkad<sup>1</sup> in studying the rainfastness of different formulations of 2,4-D [(2,4-dichlorophenoxy)acetic acid].

Another approach is to apply a parallel-line assay. As shown previously,<sup>9</sup> the influence of rain on herbicide activity can be analyzed using a parallel-line assay because the dose-response curves with and without rain can be assumed to be parallel in that rain is only affecting the amount of herbicide penetrating into the plant. Consequently, within each experiment, a parallel-line assay was run for each adjuvant by simultaneously fitting the following five-parameter nonlinear regression model expressing dry weight ( $U_i$ ) as a function of herbicide dose ( $z$ )

$$\log_e(U_i) = \log_e\{(D - C)/[1 + \exp(-2(a + b \log_{10}(R_i z)))] + C\} + e \quad (1)$$

to the three dose-response curves ("no rain" and rain 2 and 4 h after herbicide application). The parameters  $D$  and  $C$  denote the upper and lower limits at zero and large doses, respectively,  $a$  describes the horizontal location,  $b$  is proportional to the slope around  $ED_{50}$ ,  $e$  is an error term, and  $R_i$  is the relative potency of the sulfonylurea herbicides when rain is applied compared to the no-rain treatment. The relative potency expresses the ratio of the doses of the no-rain treatment and a rain treatment giving a similar effect.

A more detailed discussion of the concept of the parallel-line assay and its application in herbicide studies has been given elsewhere.<sup>7,12</sup>

The regressions were assessed by a test for lack of fit and graphical analyses of residuals.<sup>3</sup>

TABLE 1  
ED<sub>50</sub> Values of Thifensulfuron and Tribenuron  
Applied Alone or with Various Adjuvants

Adjuvant	Thifensulfuron (g ha <sup>-1</sup> )	Tribenuron (g ha <sup>-1</sup> )
	Experiment 1	Experiment 3
None	0.082 (0.019)	0.034 (0.005)
0.1% Lissapol	0.032 (0.005)	0.021 (0.002)
1% Codacide	0.024 (0.007)	0.020 (0.003)
1% Atplus 411F	0.029 (0.007)	0.018 (0.002)
2.5% Ammonium sulfate	0.107 (0.020)	0.069 (0.009)
	Experiment 2	Experiment 4
None	0.043 (0.007)	0.031 (0.003)
1% Codacide	0.024 (0.005)	0.018 (0.003)
0.025% Silwet® L77	0.025 (0.006)	0.017 (0.005)
0.5% Frigate®	0.018 (0.004)	0.022 (0.004)
0.15% Spraymate Bond	0.025 (0.007)	0.039 (0.007)

Note: Figures in parentheses are standard errors.

### III. RESULTS AND DISCUSSION

Table 1 contains the ED<sub>50</sub> values of the no-rain treatments calculated on the basis of the estimated regression parameters [ED<sub>50</sub> = antilog(-a/b)]. All adjuvants except ammonium sulfate enhanced the phytotoxicity of thifensulfuron, while ammonium sulfate and Spraymate Bond were the only adjuvants not increasing the phytotoxicity of tribenuron. Ammonium sulfate has been found to increase the efficacy of several foliage-applied herbicides, including phenoxyalkanoic acids<sup>11,14</sup> and glyphosate.<sup>2</sup> In this study, ammonium sulfate reduced the activity of tribenuron and had no effect on the phytotoxicity of thifensulfuron. Similarly, Feist and Nalewaja<sup>4</sup> found no influence of ammonium sulfate on the phytotoxicity of thifensulfuron applied alone against kochia (*Kochia scoparia*) and a reduction in activity by ammonium sulfate when thifensulfuron was applied with the surfactant X-77 or methylated soybean oil. These results indicate that the phytotoxicity of the sulfonyleurea herbicides might actually be antagonized by ammonium sulfate.

The relative potencies of the herbicides after application of rain (Tables 2 and 3) are expressed relative to the corresponding no-rain treatment. This implies that relative potency expresses the effect of the adjuvant on the rainfastness of the spray deposit and not on the phytotoxicity of the herbicide, as the latter is dependent on the herbicide dose. Improved rainfastness with an adjuvant is probably caused by an increased uptake rate and/or improved adherence to the leaf surface protecting the spray deposits against washoff by rain.

In all experiments, rain 2 and 4 h after herbicide application reduced the phytotoxicity of both thifensulfuron and tribenuron significantly when the herbicides were applied without an adjuvant (Tables 2 and 3).

Ammonium sulfate was the only adjuvant in experiment 1 which did not improve the rainfastness of thifensulfuron. When rain was applied 2 h after spraying, both 1% Codacide and 1% Atplus 411F improved rainfastness significantly more than the nonionic surfactant; however, only with Codacide was no significant reduction in herbicide activity observed by rain 2 h after spraying. No significant differences in rainfastness were found between Lissapol, Codacide, and Atplus 411F with rain 4 h after spraying and, irrespective of

**TABLE 2**  
**Relative Potencies of Thifensulfuron Applied with**  
**Various Adjuvants after Application of 3 mm of**  
**Rain 2 and 4 h after Herbicide Application**

Adjuvant	Rain after 2 h	Rain after 4 h
<b>Experiment 1</b>		
None	0.16 (0.08–0.24)	0.29 (0.16–0.43)
0.1% Lissapol	0.51 (0.35–0.69)	0.88 (0.57–1.18)
1% Codacide	0.95 (0.59–1.32)	0.98 (0.59–1.36)
1% Atplus 411F	0.74 (0.53–0.96)	0.86 (0.60–1.13)
2.5% Ammonium sulfate	0.29 (0.16–0.42)	0.39 (0.22–0.56)
<b>Experiment 2</b>		
None	0.10 (0.07–0.13)	0.23 (0.16–0.30)
1% Codacide	0.82 (0.58–1.06)	0.98 (0.70–1.26)
0.025% Silwet® L77	0.46 (0.29–0.63)	0.79 (0.48–1.10)
0.5% Frigate®	0.50 (0.32–0.67)	0.62 (0.40–0.84)
0.15% Spraymate Bond	0.95 (0.59–1.31)	0.94 (0.58–1.30)

*Note:* The relative potency of the corresponding no-rain treatment = 1.00. Figures in parentheses are approximate 95% confidence intervals.

**TABLE 3**  
**Relative Potencies of Tribenuron Applied with**  
**Various Adjuvants after Application of 3 mm of**  
**Rain 2 and 4 h after Herbicide Application**

Adjuvant	Rain after 2 h	Rain after 4 h
<b>Experiment 3</b>		
No adjuvant	0.30 (0.23–0.37)	0.43 (0.33–0.53)
0.1% Lissapol	0.64 (0.53–0.74)	0.83 (0.69–0.96)
1% Codacide	1.01 (0.79–1.23)	0.98 (0.76–1.19)
1% Atplus 411F	0.80 (0.65–0.95)	0.91 (0.73–1.09)
2.5% Ammonium sulfate	0.37 (0.28–0.47)	0.47 (0.35–0.59)
<b>Experiment 4</b>		
No adjuvant	0.19 (0.14–0.23)	0.32 (0.25–0.39)
1% Codacide	0.78 (0.62–0.93)	0.87 (0.70–1.05)
0.025% Silwet® L77	0.84 (0.63–1.05)	1.02 (0.76–1.27)
0.5% Frigate®	0.19 (0.15–0.23)	0.29 (0.23–0.35)
0.15% Spraymate Bond	0.49 (0.35–0.63)	0.58 (0.42–0.74)

*Note:* The relative potency of the corresponding no-rain treatment = 1.00. Figures in parentheses are approximate 95% confidence intervals.

adjuvant, thifensulfuron activity was not significantly reduced compared to the corresponding no-rain treatment. In the present experiment, thifensulfuron applied with a nonionic surfactant was considerably more rainfast than reported by Nalewaja and Adamczewski,<sup>10</sup> who found that 2 mm of rain within 24 h after treatment reduced the phytotoxicity to kochia (*Kochia scoparia*) of thifensulfuron applied with 0.25% of the nonionic surfactant X-77. This discrepancy could have resulted from the use of different plant species or different nonionic surfactants.

In the second thifensulfuron experiment, all adjuvants considerably increased rainfastness; however, 1% Codacide and 0.15% Spraymate Bond® were significantly more effective in improving rainfastness than were 0.025% Silwet L-77 and 0.5% Frigate. In combination with Codacide and Spraymate Bond, thifensulfuron was rainfast 2 h after herbicide application. With the addition of 0.025% Silwet® L-77, thifensulfuron was rainfast after 4 h, whereas more than 4 h was required to ensure maximum activity of thifensulfuron in combination with 0.5% Frigate®. Codacide and Spraymate Bond are claimed to improve rainfastness, and Taylor and Matthews<sup>13</sup> reported that both adjuvants increased the rainfastness of the insecticide bendiocarb on brussels sprouts (*Brassica oleracea* var. *germinifera*). Spraymate Bond is supposed to improve rainfastness mainly by increasing the resistance of the spray deposit to washoff; however, the increased phytotoxicity of the no-rain treatment of thifensulfuron plus Spraymate Bond compared to thifensulfuron alone indicates that penetration of the herbicide into the plant also is affected by this adjuvant.

The results from experiment 3 with tribenuron were very similar to those from the corresponding experiment 1 with thifensulfuron, as ammonium sulfate did not enhance rainfastness and both 1% Codacide and 1% Atplus 411F improved rainfastness significantly more than 0.1% Lissapol when rain occurred 2 h after application (Table 3). Only when tank mixed with Codacide did rain 2 h after spraying not reduce herbicide activity significantly. In contrast to the thifensulfuron experiment, a rain-free period of 4 h was not sufficient to ensure the maximum effect of tribenuron with 0.1% Lissapol, whereas addition of both Codacide and Atplus 411F resulted in full rainfastness. Kudsk et al.<sup>8</sup> found in a previous study that tribenuron was more rainfast than thifensulfuron in combination with 0.1% Lissapol. In contrast to that study, the experiments with the two herbicides were not conducted simultaneously in the present study, and as the environmental factors have been shown to affect the rainfastness of sulfonylurea herbicides,<sup>9</sup> this may explain the discrepancy between the two studies.

In experiment 4, tribenuron applied alone and with 1% Codacide was not as rainfast as in experiment 3; these results also might be attributed to differences in environmental conditions at the time of herbicide application. The influence of 1% Codacide on the rainfastness of tribenuron is illustrated graphically in Figure 1. The horizontal distances between the dose-response curves are significantly reduced when Codacide is included in the spray solution, indicating an increased rainfastness. Furthermore, Figure 1 supports the assumption that the parallel-line assay is a reasonable method for assessing the influence of rain on herbicidal activity.

The effect of 0.025% Silwet L-77 on the rainfastness of tribenuron was similar to that of Codacide. Silwet L-77 at 0.1% (v/v) has been found to increase the rainfastness of glyphosate [*N*-(phosphonomethyl)glycine] on perennial ryegrass (*Lolium perenne*) by promoting the infiltration of herbicide into the substomatal cavities.<sup>5</sup> No attempt was made to determine whether tribenuron also infiltrated into the stomata at the very low concentration of Silwet L-77 used in this study; however, based on evidence from other studies, this seems unlikely.<sup>5,15</sup>

The increased activity of both sulfonylurea herbicides caused by 0.025% Silwet L-77 (Table 1) indicates an effect on the cuticular penetration of the herbicides. Hence, improved



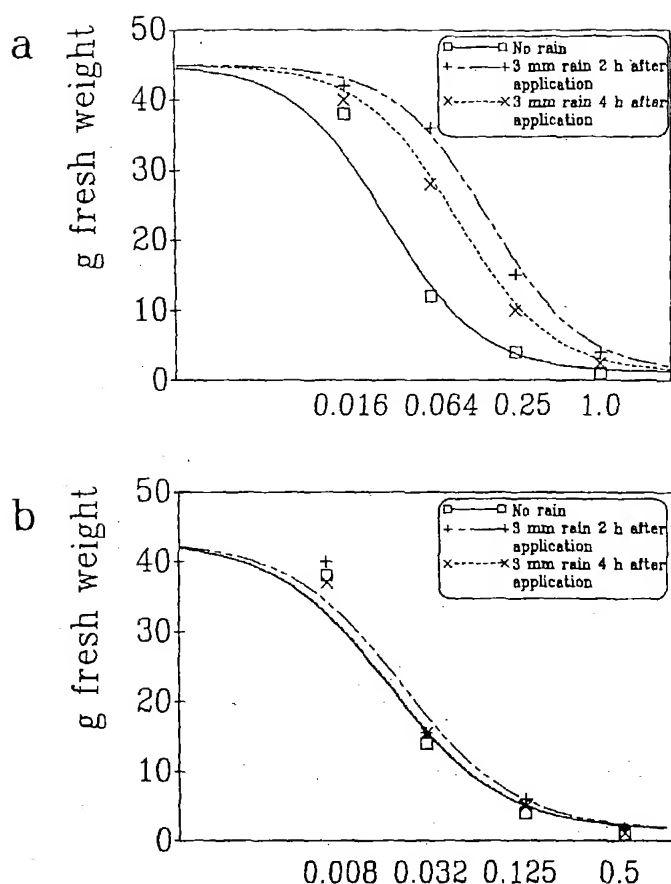


FIGURE 1. The influence of 3 mm of rain 2 and 4 h after herbicide application on the activity of (a) tribenuron applied without adjuvant and (b) tribenuron plus 1% (v/v) Codacide (results from experiment 4). The curves are the estimated dose-response curves and the markers are the recorded fresh weights.

rainfastness found with the herbicides upon addition 0.025% Silwet L-77 could be due to increased uptake during the initial hours after herbicide application. Silwet L-77 promoted the rainfastness of both herbicides, however, the effect on tribenuron was more pronounced than with thifensulfuron. Although difficult to account for, this difference might be explained by specific interactions between the herbicides and the adjuvant affecting uptake through the cuticle. The use of Silwet L-77 as an adjuvant for increasing the rainfastness of the sulfonylurea herbicides needs further study.

Addition of 0.5% Frigate did not increase the rainfastness of tribenuron, contrary to what was found with thifensulfuron. Similarly, Spraymate Bond increased the rainfastness of tribenuron substantially less than that of thifensulfuron. As seen in Table 1, whereas Frigate® and Spraymate Bond increased the activity of thifensulfuron significantly, the phytotoxicity of tribenuron was improved less by Frigate and not promoted with Spraymate Bond, indicating a correlation between the ability of the two adjuvants to increase phytotoxicity and rainfastness, respectively.

The results of the present study have confirmed those of previous experiments that, when applied without additional adjuvant, tribenuron seems to be somewhat more rainfast



than thifensulfuron, although none of the herbicides are very rainfast.<sup>8</sup> Further, the experiments have shown that, besides the ability to increase phytotoxicity, adjuvants also possess the potential for improving the rainfastness of the sulfonylurea herbicides substantially. Several of the adjuvants included in this study enhanced the phytotoxicity of the herbicides equally as well as the recommended nonionic surfactant, but had a more pronounced effect on rainfastness and could therefore be more beneficial as recommended adjuvants to thifensulfuron and tribenuron than the nonionic surfactant. However, this study has also shown that within the class of sulfonylurea herbicides, pronounced differences in the response to an adjuvant can occur, indicating that it can be misleading to transfer the results of adjuvant studies from one herbicide to another even if the herbicides are closely related structurally.

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## Chapter 43

**THE EVALUATION OF TEN EMULSIFIERS FOR USE WITH A  
MINERAL OIL ADJUVANT**

David Coupland and Sandra Robinson

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## ABSTRACT

Ten test emulsifiers and one commercial product (Actipron®, B.P. Chemicals) were evaluated as adjuvants for use with two herbicide-mineral oil-water mixtures. The two herbicides were phenmedipham and quizalofop-ethyl. Effects on emulsion stability were determined by a simple standing test and by measuring oil droplet size in the emulsion. Stability was influenced by the herbicides (and any formulation components present in the herbicide concentrates) and/or the type of emulsifier. All phenmedipham emulsions were fully stable over the 16-h experimental period, including those formulated with oil but no emulsifier. The stability of the quizalofop-ethyl mixtures, however, depended upon the type of emulsifier used. The smallest oil droplets were observed in the phenmedipham mixtures, and the type of emulsifier had no influence on this. Oil droplets in the quizalofop-ethyl mixtures were approximately 125 times larger (by volume) than those in the phenmedipham emulsions, and none of the test emulsifiers produced droplets smaller than those formed using Actipron. The influence of emulsifier on herbicide efficacy was determined by spraying *Chenopodium album* L. (common lambsquarters) and *Hordeum vulgare* L. (barley) with phenmedipham and quizalofop-ethyl emulsions, respectively. Phenmedipham performance was significantly improved by five of the test emulsifiers, whereas, with quizalofop-ethyl, only two test emulsifiers enhanced performance compared with the Actipron treatment. *In vivo* and *in vitro* tests established that none of the test emulsifiers was phytotoxic to a typical broadleaved crop species *Beta vulgaris* L. (sugar beet).

## I. INTRODUCTION

Herbicides are formulated as emulsifiable concentrates for a number of reasons. If the active ingredient (a.i.) is water insoluble, then an emulsifying system is used to disperse the herbicide in the aqueous carrier. Other herbicides are formulated as emulsifiable concentrates even though the a.i. is partially water soluble. Examples of this type of compound are fluazifop-*p*-butyl{(R)-butyl 2-[4-[[5-trifluoromethyl]-2-pyridinyl]oxy]phenoxy]propanoate}, quizalofop-ethyl {ethyl(±)-2-[4-[(6-chloro-2-quinoxalinyloxy]phenoxy]propanoate}, and flumetypal-methyl {methyl[N-benzoyl-N-(3-chloro-4-fluorophenyl)-DL-alanine]}, de-esterification producing the a.i. Although there are exceptions, e.g., diclofop-methyl {(±)-2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid},<sup>10</sup> these esters are generally not considered phytotoxic, but are used because they permeate plant cuticles more readily than the polar, more hydrophilic parent herbicide acids and are readily hydrolyzed, thus "delivering" the a.i. inside the plant.<sup>4</sup> Finally, the use of certain spray additives, in particular oil adjuvants, also necessitates the use of emulsifiers. For herbicides that are water insoluble and require an oil adjuvant, the choice of an effective emulsifying system is of paramount importance. Oils are used as additives for various reasons, such as reducing vapor loss, enhancing performance on weed species that are not normally controlled well by the herbicide alone, and in situations which are likely to reduce herbicide efficacy, such as poor weather conditions.<sup>3,8,9</sup> Oils of various types are used, although refined vegetable and mineral oils are the most common.<sup>7</sup> This chapter describes the evaluation of ten emulsifiers manufactured by Croda Universal Limited (Hull, England) for use with a mineral oil adjuvant. Compounds were compared using three criteria: emulsion stability, phytotoxicity, and effect on the performance of two herbicides, phenmedipham {3-[(methoxycarbonyl)amino]phenyl(3-methylphenyl)carbamate} and quizalofop-ethyl. Both of these herbicides are recommended for use in *B. vulgaris* and both require an oil adjuvant under normal field use for optimum effect.\*

\* Technical Product Information, Schering Agriculture, Nottingham, England.

## II. MATERIALS AND METHODS

### A. PLANTS

Single plants were grown in 9-cm pots under greenhouse conditions. *B. vulgaris* var. Samson was treated at the four-leaf stage, *Chenopodium album* at the four- to six-leaf stage, and *Hordeum vulgare* var. Golden Promise, representing a volunteer graminaceous weed, at the three- to four-leaf stage.

### B. HERBICIDES

Phenmedipham and quizalofop-ethyl (ethyl ester) were obtained from Schering Agrochemicals Limited (Saffron Waldon, England) as emulsifiable concentrates containing 114 and 500 g a.i. l<sup>-1</sup> respectively.

### C. EMULSIFIER AND OIL PROPERTIES

Properties of the ten test emulsifiers used in this work are shown in Table 1. These compounds were compared with a recommended oil adjuvant, Actipron, which was supplied by B. P. Research International, Sunbury-on-Thames, England as a 3% solution of emulsifier (undisclosed chemistry) in mineral oil (also supplied by B. P. Research International). All candidate emulsifiers were dissolved or dispersed in the base oil at 3% (w/v) concentration. Base oil properties were as follows: viscosity (at 40°C), 30 cSt; flash point (PMC), 210°C; density (at 15°C), 0.875; molecular weight, 403 (data supplied by B. P. Oil Limited, England).

### D. SPRAYING

Spray solutions were prepared by adding the required amount of oil-emulsifier to half the volume of distilled water and, after manually shaking for 2 min, adding the required amount of herbicide concentrate. Typically, oil adjuvants were used at 21 ml (of the 3% emulsifier mixture) l<sup>-1</sup> of spray solution. The remainder of the water was then added to volume and the mixture shaken vigorously for 5 min before use. Plants were sprayed using a laboratory track sprayer fitted with a single Spraying Systems 8001 "T-jet" nozzle delivering the equivalent of 240 l ha<sup>-1</sup>.

### E. MEASUREMENT OF EMULSION STABILITY

#### 1. Standing Tests

Emulsions were prepared by adding 0.42 ml of the oil-emulsifier mixture to 20 ml of distilled water. This was equivalent to the recommended field rate for Actipron of 5 l ha<sup>-1</sup>. When included, herbicides were also used at their recommended field rates of 1.14 kg a.i. ha<sup>-1</sup> (phenmedipham) and 125 g a.i. ha<sup>-1</sup> (quizalofop-ethyl). Each treatment was prepared in 30-ml parallel-sided glass bottles with screw tops and shaken vigorously for 10 min on a wrist-action shaker. After standing for 1 and 16 h, respectively, measurements were taken of the depths of any distinct layers. Emulsions were then subjectively scored by visual observation using a scale of 0 to 4 (most stable to least stable). All tests were carried out in a temperature-controlled room at 20°C, and all measurements were performed three times.

#### 2. Oil Droplet Size

Samples of emulsions, prepared as in Section II.E.1, were examined immediately after shaking. For the phenmedipham mixtures, a small drop of liquid was placed under a single cover slip on a microscope slide. For those without herbicide, or for the quizalofop-ethyl mixtures, a larger quantity of liquid was needed because of the larger, and fewer, oil droplets

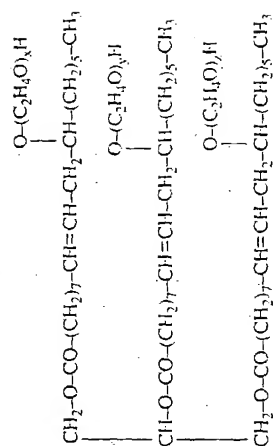


TABLE I  
Emulsifier Properties and Treatment Codes

Treatment code no.	Commercial name	Chemical name	Formula	HLB	Appearance	Appearance of oil/emulsifier mixture
E1	Crodet S4	Ethoxy (4) stearic acid	$R-CO-O-(CH_2)_7-(O-C_2H_4)_x-OH$ , where $R = \text{stearyl}$	7.7	White, soft solid	Cloudy dispersion
E2	DGMO	Diglycerol mono-oleate	$HOCH-CH(OH)-CH_2-O-CH_2-CH(OH)-CH_2-O-R$ , where $R = \text{oleyl}$ ( $C_{18}$ ); a mixture of monoesters at positions 1, 2, 5, and 6	3-6	Yellow liquid	Clear solution
E3	Crodet O4	Ethoxy (4) oleic acid	$R-COO-(CH_2)_7-(O-C_2H_4)_x-OH$ , where $R = \text{oleyl}$	7.7	Yellow/amber liquid	Cloudy dispersion
E4	Volpo N3	Ethoxy (3) oleyl alcohol	$R-(O-C_2H_4)_3-OH$ , where $R = \text{oleyl}$	6.6	Pale yellow liquid	Slightly cloudy dispersion
E5	Croduret 10	Ethoxy (10) hydrogenated castor oil		6.3	Pale yellow liquid	Cloudy dispersion
E6	Etocas 20	Ethoxy (20) castor oil	$  \begin{array}{c}  \text{O}-(C_2H_4O)_xH \\    \\  CH_2-O-CO-(CH_2)_{10}-CH-(CH_2)_5-CH_3 \\    \\  CH-O-CO-(CH_2)_{10}-CH-(CH_2)_5-CH_3 \\    \\  CH-O-CO-(CH_2)_{10}-CH-(CH_2)_5-CH_3  \end{array}  $	9.6	Pale yellow liquid	Slightly cloudy dispersion

where  $(x + y + z) = 10$ , average no. moles of ethylene oxide per mole of castor oil.





where  $(x + y + z) = 20$

E7	Etocas 10	Ethoxy (10) castor oil	As above, $(x + y + z) = 10$	6.3	Pale yellow liquid	Slightly cloudy dispersion
E8	Volpo N10	Ethoxy (10) oleyl alcohol	$\text{R}-(\text{O}-\text{C}_2\text{H}_4)_x-\text{OH}$ , where R = oleyl	12.4	Pale yellow paste	Cloudy dispersion
E9	Base oil	Mineral oil	—	—	—	Clear liquid
E10	Actipron	Mineral oil + emulsifier	Undisclosed chemistry	—	—	Clear solution
E11	Crodet S8	Ethoxy (8) stearic acid	$\text{R}-(\text{CO}-\text{O}-\text{CH}_2)_2-(\text{O}-\text{C}_2\text{H}_4)_x-\text{OH}$ , where R = stearyl	10.8	Off-white soft paste	Cloudy dispersion
E12	Volpo N5	Ethoxy (5) oleyl alcohol	$\text{R}-(\text{O}-\text{C}_2\text{H}_4)_x-\text{OH}$ , where R = oleyl	9.0	Pale yellow liquid	Slightly cloudy dispersion

which were formed (the cover slip being supported at each side by two more cover slips). Each sample was examined using Zeiss Nomarski interference optics and a  $100\times$  oil-immersion objective lens. Three photographs of randomly selected areas from each sample were taken, a graticule being used for calibration purposes. Photographs were covered with a template and oil droplets within the template area were measured. In this way, nonsubjective measurements could be made. Templates for the phenmedipham treatments had five  $5\times 3$ -cm sampling areas, while those for the other mixtures had one of  $10\times 7.5$  cm in order to accommodate better the larger sizes of droplet. An Optimax Image Analyser was used to measure oil droplet diameter.

## F. PHYTOTOXICITY TESTS

### 1. Whole Plant Response

Emulsions were prepared without herbicides as described above. *H. vulgare*, *C. album*, and *B. vulgaris* plants were sprayed with these mixtures and assessed for any visible signs of foliar damage periodically over 14 d; shoot fresh weights were then measured. To overcome any possible differences in spray retention, mixtures were also applied as discrete droplets to single leaves of *B. vulgaris* using a microsyringe. Forty  $1\text{-}\mu\text{l}$  droplets were dispensed evenly over the leaf surface, which was visually assessed for damage over the next 14 d.

### 2. Potassium Efflux Bioassay

*B. vulgaris* leaf discs were incubated in each of the test emulsions (*in vitro* tests). Three  $1.5\text{-cm}$  diameter discs were taken using a cork borer, washed in distilled water for about 10 min to remove electrolytes from the cut surfaces, then incubated in 50 ml of the test emulsions. Each oil-emulsifier mixture was used at  $21\text{ ml}$  (of the 3% mixture)  $\text{l}^{-1}$  equivalent to the recommended field rate for Actipron. Flasks were gently agitated on an orbital shaker for 24 h in the light. Samples ( $1\text{ ml}$ ) of each emulsion were taken for potassium analysis, using flame photometry before and after incubation. The leaf discs were then homogenized in the remainder of the bathing solution, using an Ultra-Turrax vortex blender. One-milliliter aliquots of the homogenates were filtered through cotton wool before making potassium ion determinations, as described above. Potassium efflux was expressed as a percentage of the total potassium ion concentration:

$$\frac{24\text{-h value} - \text{zero-time value}}{\text{total value} - \text{zero-time value}} \times 100$$

## G. CROP SAFETY

*B. vulgaris* plants were sprayed with phenmedipham formulated with each of the oil-emulsifier mixtures, all components of the spray solution being used at their recommended field rates (see above). Plants were kept under greenhouse conditions for 24 h after treatment; then, four leaf discs were taken (two from each of the larger pair of leaves from each plant) and placed in 50 ml of distilled water (*in vivo* tests). Potassium efflux was determined as before.

## H. HERBICIDE EFFECTIVENESS

*C. album* plants were sprayed with phenmedipham at 0, 0.2, 0.4, 0.6, and  $0.8\text{ kg a.i. ha}^{-1}$ , and barley plants with quizalofop-ethyl at 0, 12, 24, 36, 48, and  $60\text{ g a.i. ha}^{-1}$ . When present, the oil-emulsifier adjuvant was kept constant at an amount equivalent to  $5\text{ l ha}^{-1}$ . For each experiment, a set of plants was sprayed with herbicide only (no oil or emulsifier), another set was treated with only the oil-emulsifier adjuvants (no herbicide), and a third set

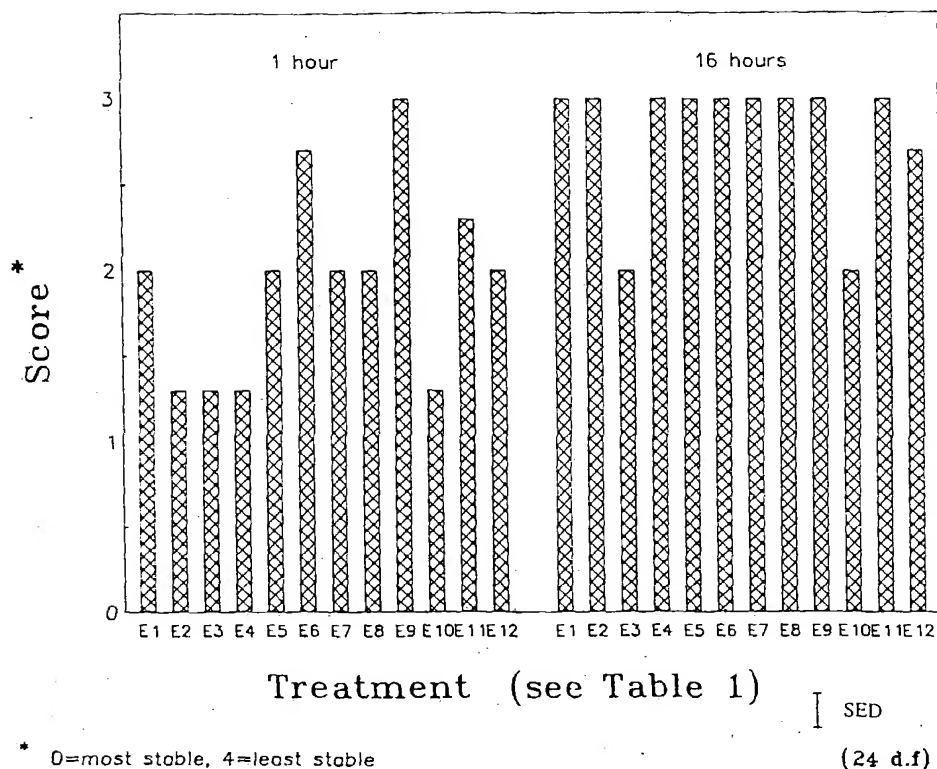


FIGURE 1. Visual assessment of the stability of quizalofop-ethyl emulsions. SED, standard error difference; d.f., degrees of freedom.

with base oil and herbicide (no emulsifier). After spraying, all plants were placed in a randomized block in the greenhouse. After 14 d, fresh shoot weights were measured. All treatments had four replicates.

### I. STATISTICAL ANALYSIS

All data were subjected to analyses of variance. Data transformation was necessary in order to compare some treatment means (see Figures).

## III. RESULTS AND DISCUSSION

### A. EMULSION STABILITY

The presence of the a.i. clearly had a profound effect on emulsion stability. Mixtures containing phenmedipham were fully stable over 16 h, even those with oil but no emulsifier (data not presented), whereas those containing quizalofop-ethyl began to break down within 1 h of mixing (Figure 1). This interaction could have been due to the a.i. itself, or the presence of other emulsifiers and/or solvents in the herbicide concentrates. This information was not provided by the suppliers, but the phenmedipham concentrate contained at least one organic solvent, tentatively identified by GC analysis as isophorone (3,5,5-trimethyl-2-cyclohexene-1-one). While the presence of organic solvent may help with emulsion stability, undesirable phytotoxic effects on plant cells have been found.<sup>2</sup> As expected, when emulsifier was not included in the mixture, stability was poor and emulsions began to break down within minutes of mixing. The no-herbicide treatments allowed a more direct comparison

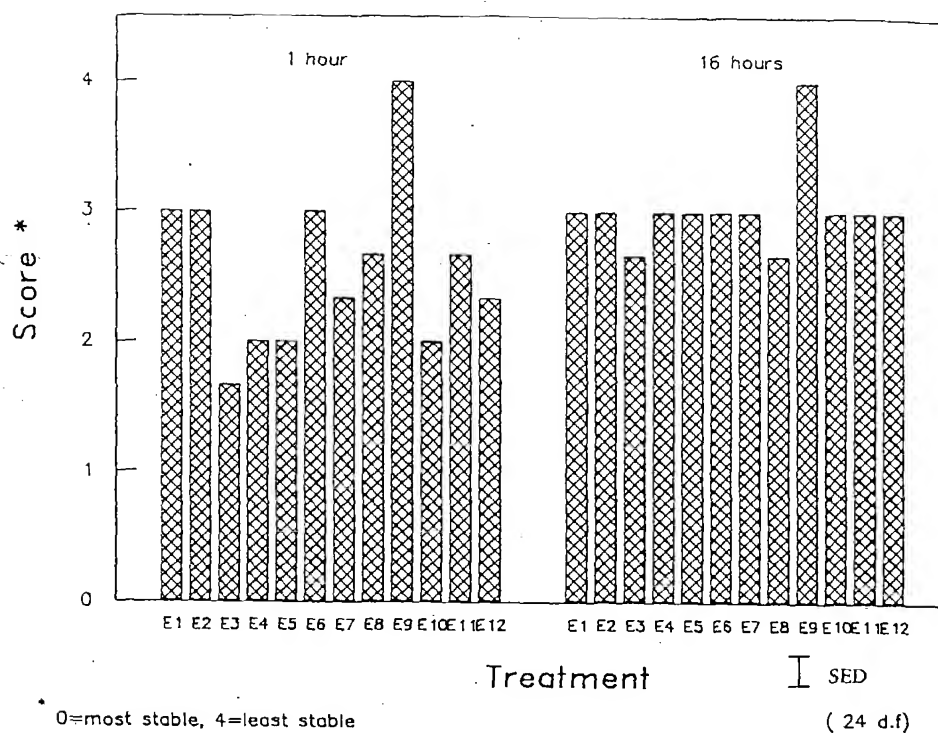


FIGURE 2. Visual assessment of the stability of no-herbicide emulsions. SED, standard error difference; d.f., degrees of freedom.

between emulsifiers and showed that compounds E3, E4, and E5 were as effective as the Actipron adjuvant (Figure 2). Phase separation was quantitatively determined in these no-herbicide mixtures by measuring the depth of the aqueous layers formed after standing (Figure 3). At 1 h after mixing, treatments E8 and E9 were significantly less stable than the others, while at 16 h, emulsions formed by E7, E8, E9, and E11 were the least stable.

Emulsions containing phenmedipham had smaller oil droplets than those containing quizalofop-ethyl or no herbicide (Table 2). Although oil droplet size was closely correlated with emulsion stability, the most unstable mixtures, i.e., those including oil but no emulsifier, did not contain the largest oil droplets. This may have been due to the difficulty of obtaining a representative sample of these unstable emulsions, even though they were sampled as quickly as possible after mixing. A more accurate method, using photon correlation spectroscopy, has recently been described by Hill.<sup>5</sup>

In order to be useful, oil adjuvants must be readily emulsifiable, and the emulsions need to remain stable for at least the time it takes to apply the herbicide to the foliage. Of these two criteria, the first is more important as it usually takes only a few seconds, at most, for the spray to leave the nozzles and be intercepted by the foliage. The stability data indicate that emulsion breakdown is unlikely to be a problem with any of the emulsifiers tested.

## B. PHYTOTOXICITY TESTS

None of the oil-emulsifier mixtures was toxic to any of the test plants when applied to foliage as a spray or discrete droplets. Localized phytotoxicity has been reported, for example, when surfactants were applied as droplets to *Vigna unguiculata* (L.) (cowpea) leaves.<sup>6</sup> A more severe test of phytotoxicity was the *in vitro* potassium leakage bioassay, where leaf

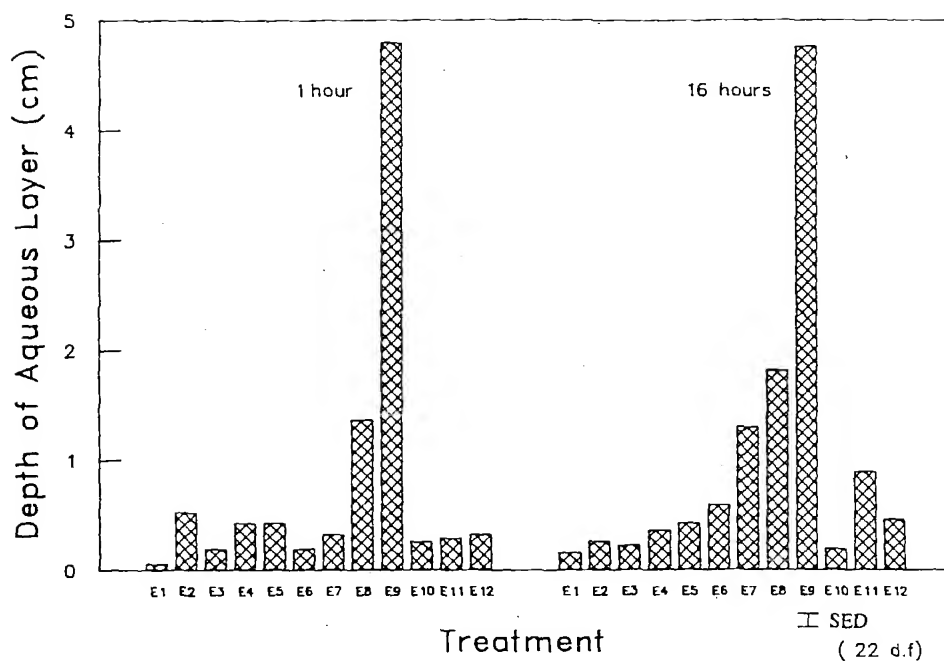


FIGURE 3. Relative instability of no-herbicide emulsions. SED, standard error difference; d.f., degrees of freedom.

TABLE 2  
Influence of Emulsifier on Mean Oil Droplet Diameter

Emulsifier*	Mean oil droplet size ( $\mu\text{m}$ )		
	Phenmedipham mixture	Quizalofop-ethyl mixture	No herbicide
E1	1.07	4.80	5.06
E2	0.74	4.19	4.81
E3	0.81	4.28	3.54
E4	0.95	4.27	3.87
E5	1.10	4.68	4.49
E6	0.92	5.41	6.36
E7	0.88	4.01	5.11
E8	0.86	5.68	5.36
Base oil only (E9)	1.07	3.89	4.18
E10	0.96	3.52	4.57
E11	1.07	5.52	4.70
E12	1.12	4.66	4.01
SED (22 d.f.)	0.108	0.825	1.195

\* See Table 1 for information on emulsifiers.

discs were completely immersed in the emulsions. Only Actipron caused more leakage than water alone (Table 3).

### C. CROP SAFETY

Toxicity of the emulsions containing phenmedipham to *B. vulgaris* leaves was investigated using the *in vivo* potassium leakage bioassay (Table 3). None of the emulsions was



TABLE 3  
Potassium Leakage from *B. vulgaris* Leaf  
Discs Treated with Test Emulsifiers  
(*in vitro*) or Phenmedipham Emulsions  
(*in Vivo*)

Treatment	% Leakage	
	<i>In vivo</i>	<i>In vitro</i>
E1	9.3	6.6
E2	8.0	0.9
E3	7.3	3.3
E4	8.8	0.6
E5	7.5	3.0
E6	8.7	4.0
E7	9.3	5.3
E8	7.5	6.1
Base oil only (E9)	9.4	2.9
E10	9.7	10.6
E11	8.9	8.3
E12	8.4	7.2
Water control	7.7	2.5
Herbicide only <sup>a</sup>	9.4	—
SED	1.44 (26 d.f.)	2.91 (48 d.f.)

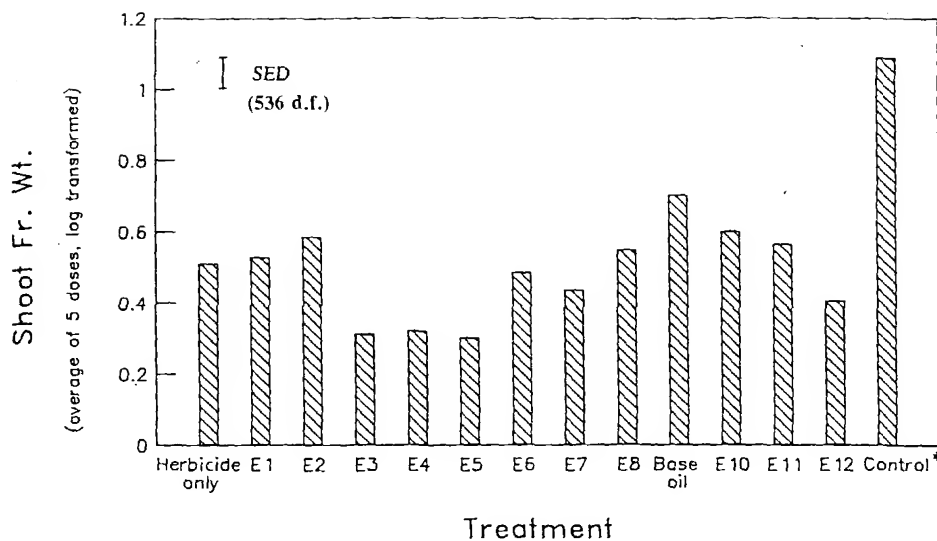
Note: *In vivo* tests used leaf discs from plants sprayed with phenmedipham and oil additives. *In vitro* tests used leaf discs immersed in oil-emulsifier/water mixtures without herbicide (see text for further details). SED is standard error difference; d.f., degrees of freedom.

<sup>a</sup> No oil or emulsifier added.

any more phytotoxic than the water controls, in agreement with the other phytotoxicity data. Other experiments established that quizalofop-ethyl was nonphytotoxic against *B. vulgaris* even when used *in vitro*, i.e., leaf discs totally immersed in the herbicide mixtures. In contrast, all phenmedipham emulsions (with or without oil adjuvant) were very toxic to leaf discs (approximately 100% potassium leakage) when used *in vitro* (data not presented).

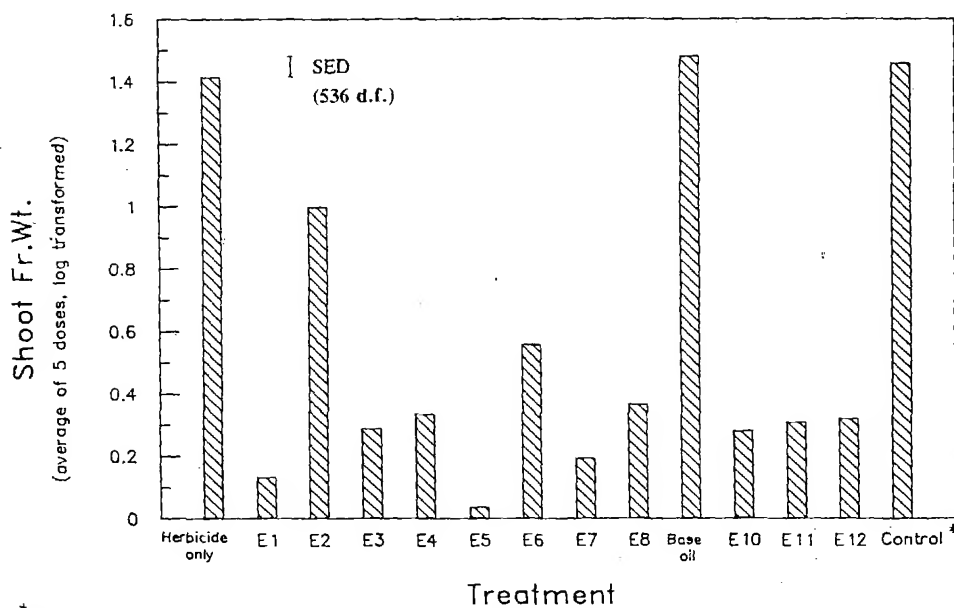
#### D. HERBICIDE EFFECTIVENESS

The influence of emulsifier on herbicide performance was determined for two compounds with contrasting modes of action. Phenmedipham is a photosynthesis inhibitor<sup>11</sup> used for the control of broadleaved weeds, whereas quizalofop-ethyl is a graminicide, the mode of action of which has not been determined, but it belongs to the oxyphenoxypionate class of herbicides which inhibit the enzyme acyl-CoA carboxylase.<sup>13</sup> Of the ten emulsifiers evaluated, five (E3, E4, E5, E7, and E12) were significantly more effective than the Actipron adjuvant in enhancing phemedipham performance; no emulsifier was significantly less effective (Figure 4). In contrast, only two emulsifiers (E1 and E5) were more effective than Actipron in enhancing quizalofop-ethyl performance, and two (E2 and E6) were significantly less effective (Figure 5). The only emulsifier to enhance the performance of both herbicides was E5, ethoxy (10)-hydrogenated castor oil having a hydrophile-lipophile balance (HLB) of 6.3. This value falls outside the recommended HLB range of 8 to 18 normally used for



\* Average of all 'no herbicide' treatments.

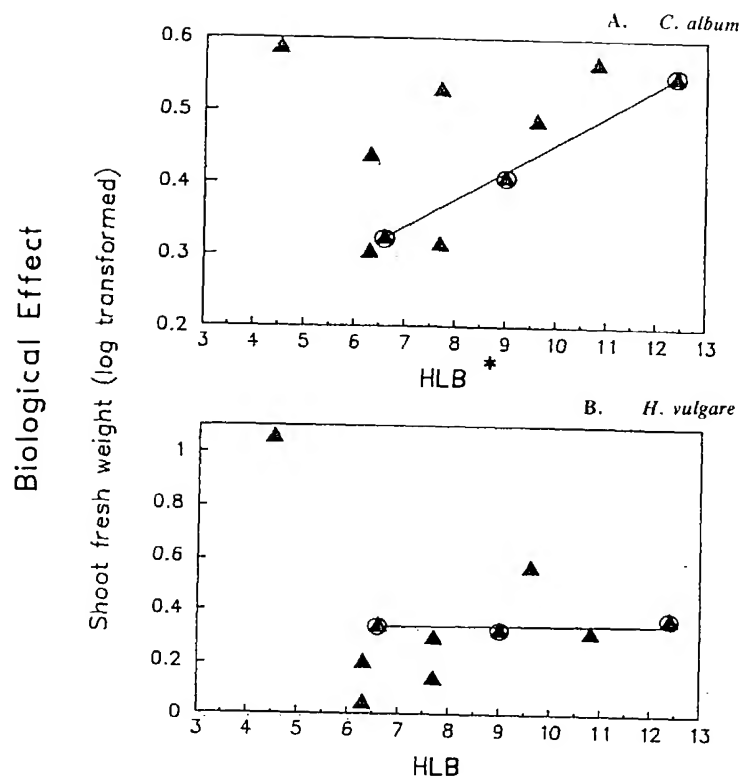
FIGURE 4. Effect of emulsifier type on the performance of phenmedipham against *Chenopodium album*.



\* Average of all 'no herbicide' treatments.

FIGURE 5. Effect of emulsifier type on the performance of quizalofop-ethyl against *Hordeum vulgare*.

producing stable oil-in-water emulsions.<sup>1</sup> However, it is well recognized that the most stable emulsions are not necessarily the most effective. Furthermore, even when emulsifiers are chosen within the optimum HLB range described above, emulsion stability can vary considerably. For example, Wakerly et al.<sup>12</sup> evaluated 14 compounds having HLB values in the



The three compounds circled are E4, E8 and E12

(see discussion for further details)

\* HLB = hydrophilic/lipophilic balance

FIGURE 6. Relationship between emulsifier HLB and biological effect.

range of 9.7 to 14.2 for the emulsification of three vegetable oils in water; emulsion stability varied from "bad" to "excellent", with no correlation to the HLB of the emulsifier used.

In the present study, we found no correlation between HLB value and biological effect (Figure 6). However, it must be stressed that the compounds tested did not constitute a "logical series", and we did not expect to find any firm relationship between emulsifier type and biological effect. Nevertheless, the series of Volpo®\* compounds (E4, E8, and E12) were chemically similar (oleyl alcohol ethoxylates); their effects on herbicide efficacy are highlighted in Figure 6. Although there was no correlation between HLB and performance for the quizalofop-ethyl series, there appeared to be a negative relationship for mixtures with phenmedipham, where an increase in HLB in the range of 6.6 to 12.4 resulted in a decrease in herbicide efficacy.

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\* Trademark of Croda Universal Limited, U.K.

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## Chapter 44

RELATIVE WAX SOLUBILITY AND PHYTOTOXICITY OF OIL  
TO GREEN FOXTAIL [*SETARIA VIRIDIS* (L.) BEAUV.]

Frank A. Manthey and John D. Nalewaja

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## ABSTRACT

Experiments were conducted to determine the relative wax solubility and phytotoxicity of various oils as influenced by emulsifier. Alkane-esterified fatty acids from vegetable oil were more soluble than once-refined vegetable oil or petroleum oil in green foxtail epicuticular leaf wax. Emulsifiers varied in their influence on an oil's solubility in the epicuticular wax. Green foxtail leaf-cell membrane permeability, as determined by electrolyte leakage from leaf disks, was increased by treating the leaves with methyl-esterified fatty acids of vegetable oil, but not by once-refined vegetable oil. Electrolyte leakage was increased by linseed oil fatty acid ethyl or butyl esters, but not by cottonseed or sunflower oil fatty acid ethyl or butyl esters. Emulsifiers with oils varied in their enhancement of electrolyte leakage from green foxtail leaves compared to oils alone. Green foxtail injury from oils correlated positively with electrolyte leakage from leaf disks, but did not correlate with relative wax solubility.

## I. INTRODUCTION

Oils are used in pesticide formulations and in pesticide application as spray adjuvants and spray carriers to aid in the foliar absorption of the pesticide. Published information is limited concerning the efficacy of pesticides formulated in vegetable oil compared to petroleum oil. However, petroleum-based oils and vegetable-based oils have been shown to differ in their effectiveness as pesticide spray adjuvants and spray carriers.<sup>1,9,14</sup>

Foliar absorption involves the passage of a pesticide through the cuticle, the cell wall, and the cell membrane. Cuticular waxes and the cell membrane are generally nonpolar, while cutin and the cell wall generally are polar. Thus, foliar absorption involves passage of the pesticide across polar and nonpolar barriers.

Oils probably enhance pesticide absorption by altering the cuticular wax and cell membrane barriers. Oils and surfactants have been reported to solubilize epicuticular leaf wax<sup>4,5,8,13</sup> and increase cell membrane permeability.<sup>2,5,12</sup>

Petroleum solvents apparently differ in their rate of wax solubilization<sup>8</sup> and in their effect on cell membrane permeability.<sup>5,12</sup> Certain petroleum solvents have been reported to increase cell membrane permeability as quickly as 2.5 min, while others had no effect after 24 h.<sup>5,12</sup> Surfactants and oils can be phytotoxic. Petroleum oils that were phytotoxic increased cell membrane permeability; however, not all oils that increased cell membrane permeability were visibly phytotoxic.<sup>5</sup>

Vegetable-based oil effects on plant cuticle and leaf cell membrane permeability are not well documented. This information would be useful in determining the effectiveness of petroleum-based oils and vegetable-based oils as spray adjuvants and spray carriers.

The objectives of this research were to determine the relative wax solubility and phytotoxicity to green foxtail of various oils as influenced by emulsifier.

## II. MATERIALS AND METHODS

### A. RELATIVE WAX SOLUBILITY

Epicuticular wax was removed from green foxtail leaves by a 10-s chloroform dip.<sup>10</sup> The chloroform was filtered to remove debris. Acetone was added to the chloroform, which precipitated the wax, while nonwax components and pigments remained dissolved in the acetone.<sup>3</sup> The acetone was filtered and the precipitate dissolved in chloroform to a concentration of 15 mg/ml. One 50- $\mu$ l droplet of chloroform-wax solution was placed on a glass microscope slide and allowed to dry for at least 24 h. The relative solubility of oil in the

TABLE 1  
Relative Wax Solubility Ratings for Oils at Various Times in  
Green Foxtail Wax

Oil	Time (min)								Mean
	0	2.5	5	10	20	40	60	1440	
Petroleum	1.0	1.0	1.0	1.0	1.3	1.3	3.8	4.5	1.9
Sunflower (sun)	1.0	1.0	1.0	1.0	1.0	1.2	2.0	3.0	1.4
Methylated Sun	1.2	2.2	2.7	3.3	4.5	5.0	5.3	5.0	3.6
Distilled water	1.0	1.3	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Note: Evaluation scale: 1.0, no solubility; 3.0, smeared circle where oil droplet was placed; 5.0, clear circle where oil droplet was placed; 7.0, smeared oblong where oil droplet was placed and drained off; 9.0, clear oblong where oil droplet was placed and drained off.

Least significant difference (LSD), 0.05; oil by time, 0.7; oil, 0.3; and time, 0.4.

epicuticular wax was determined by placing a 3- $\mu$ l droplet of oil on the wax. The slide was tilted after various times and tapped to aid drainage of the more viscous oils off the wax. The wax was then firmly wiped perpendicular to the oil drainage and a relative wax solubility number was assigned. The rating scale was from 1 to 9, where 1 = no solubility, 3 = smeared circle where the oil droplet was placed, 5 = clear circle where the oil droplet was placed, 7 = smeared oblong where the oil droplet was placed and drained off, and 9 = clear oblong where the oil droplet was placed and drained off. The experiments were conducted as a split-plot design, where the whole plots were time and subplots were oil treatments, and had six replications.

#### B. LEAF-CELL MEMBRANE PERMEABILITY

Green foxtail was grown in the greenhouse during the winter and early spring of 1989. Green foxtail was seeded in 0.5-l plastic pots and thinned to four plants per pot 1 week after emergence. Plants were watered daily as needed.

Oils were foliarly applied as spray carriers (without any water) at 9.4 l/ha, using an air brush sprayer, to green foxtail in the five-leaf stage. The air brush sprayer was calibrated for each solvent by varying orifice size and air pressure. Oil-emulsifier combinations applied as spray carriers contained 15% (v/v) emulsifier. Distilled water-emulsifier combinations applied as spray carriers contained 1.5% (v/v) emulsifier.

Twenty 0.6-mm diameter disks, five from the fourth leaf of four green foxtail plants in a pot, were punched 2.5 min, 60 min, and 24 h after treatment. The leaf disks were incubated in 20 ml of distilled water at 20°C and shaken at 90 rpm for 6 h. Electrolyte leakage was measured with a conductivity bridge using a conductivity cell ( $k = 1.0$ ). Visual green foxtail injury ratings, where 0 = no injury and 100 = complete kill, were taken 24 h after treatment. The experiments were conducted as a split-plot design, where the whole plots were time and subplots were oil treatments, and had ten replications. Procedural experiments indicated that the solvents, emulsifiers, and solvent-emulsifier combinations did not affect the electroconductivity readings of the incubation solutions.

### III. RESULTS AND DISCUSSION

#### A. RELATIVE WAX SOLUBILITY

Relative wax solubility values for petroleum, sunflower, and methylated sunflower oils increased with time (Table 1). The rate of wax solubilization was methylated sunflower  $\gg$

petroleum > sunflower oil. Significant solubilization of green foxtail leaf wax occurred within 2.5 min for methylated sunflower oil and within 60 min for petroleum oil and sunflower oil. Green foxtail leaf wax solubilization was greater with methylated sunflower oil and petroleum oil than with sunflower oil after 24 h.

Petroleum oil, sunflower oil, and methylated sunflower oil differ in their physical and chemical properties. Methylated sunflower oil was less viscous and more polar than the petroleum or vegetable oil used in this research. The viscosity (at 40°C) of methylated sunflower oil was 4 cSt; that of petroleum oil and sunflower oil was 21 and 35 cSt, respectively. Relative wax solubility of an oil has been correlated positively with polarity and negatively with viscosity.<sup>8</sup>

The crop origin — canola (*Brassica campestris* L.), cotton (*Gossypium hirsutum* L.), flax (*Linum usitatissimum* L.), rape (*Brassica napus* L.), safflower (*Carthamus tinctorius* L.), soybean [*Glycine max* (L.) Merr.], and sunflower (*Helianthus annuus* L.) — of the oils did not affect their relative solubility in green foxtail leaf wax, as once-refined or methyl-esterified vegetable oils (data not presented).

The rate of leaf wax solubilization may influence the effectiveness of an oil as a spray carrier and/or spray adjuvant. Methylated vegetable oil was equally as, or more effective than petroleum oil, and both were more effective than vegetable oil as spray adjuvants for several foliarly applied herbicides.<sup>9</sup> The solubility of oil in leaf wax may affect pesticide absorption, particularly if the pesticide is soluble in the oil. For example, fluazifop, being more soluble in vegetable oil than in petroleum oil, was absorbed and translocated more when applied with petroleum oil than with sunflower oil.<sup>11</sup> Vegetable oil, having a lower wax solubility than petroleum oil, probably transverses the cuticle slower than petroleum oil, which may account for the slower absorption of fluazifop applied with vegetable oil than with petroleum oil.

Methyl, ethyl, and butyl esters of fatty acids from vegetable oils had greater solubility in green foxtail leaf wax than their triglycerides (once-refined vegetable oil) (Table 2). Crop origin generally did not affect the relative wax solubility of once-refined, methyl, ethyl, or butyl esters of vegetable oil. The relative wax solubility for linseed and methylated linseed oil was less than for sunflower and methylated sunflower oil. The differences between linseed and sunflower oil were small and probably not of any practical importance.

Oils with and without an emulsifier differed in their relative solubility in green foxtail leaf wax, depending on the oil and emulsifier (Table 3). Atplus® 300F and T-Mulz® A02 emulsifiers in petroleum oil increased relative wax solubility values compared to petroleum oil alone after 60 min of exposure, although after 24 h (1440 min), all petroleum oil-emulsifier combinations had similar relative wax solubility values. T-Mulz A02 in sunflower oil enhanced relative wax solubility values. T-Mulz A02 in sunflower oil enhanced relative wax solubility at 60 min, but not at 24 h, compared to sunflower oil alone. Atplus 300F, T-Mulz A02, and Triton® X-45 reduced sunflower oil relative wax solubility compared to sunflower oil alone after 24 h of exposure. Emulsifier generally did not influence the solubility of methylated sunflower oil in green foxtail leaf wax regardless of the time of exposure of the oil to the wax. However, relative wax solubility of methylated sunflower oil in green foxtail leaf wax was enhanced with Atplus 300F 2.5 min after exposure, but by 24 h, all methylated sunflower oil-emulsifier combinations were similar. Thus, oil solubility in leaf wax can be increased, decreased, or not affected by the presence of an emulsifier.

The effectiveness of an oil as a herbicide spray adjuvant or carrier can be affected by the emulsifier present in the oil.<sup>6,7</sup> The emulsifier effect on the relative wax solubility of an oil may be important in determining the effectiveness of an oil as a pesticide spray adjuvant or spray carrier, but the magnitude of importance is not known. Emulsifiers in an

TABLE 2  
Relative Wax Solubility Ratings for Once-Refined and  
Alkane-Esterified Oils of Various Crop Origins in  
Green Foxtail Wax, Averaged Over Time

Oil type	Crop origin			Mean
	Cottonseed	Linseed	Sunflower	
Triglyceride	1.6	1.4	1.8	1.6
Methyl ester	3.9	3.7	4.0	3.9
Ethyl ester	3.9	3.7	3.7	3.8
Butyl ester	3.9	3.9	3.7	3.8
Mean	3.3	3.2	3.3	—

Note: Evaluation scale: 1.0, no solubility; 3.0, smeared circle where oil droplet was placed; 5.0, clear circle where oil droplet was placed; 7.0, smeared oblong where oil droplet was placed and drained off; 9.0, clear oblong where oil droplet was placed and drained off.

LSD, 0.05; oil type by crop origin, 0.3; oil type, 0.2; crop origin, not significant.

TABLE 3  
Relative Wax Solubility of Oils in Green Foxtail Wax  
as Influenced by Emulsifiers

Oil	Emulsifier	Time (min)			Mean
		2.5	60	1440	
P011N	None	1.0	1.5	5.0	2.5
P011N	Atplus 300F	1.0	3.8	5.0	3.3
P011N	T-Mulz A02	1.2	3.7	5.0	3.3
P011N	Triton® X-45	1.0	1.0	5.0	2.3
Sunflower	None	1.0	1.0	3.3	1.8
Sunflower	Atplus 300F	1.0	1.0	2.5	1.5
Sunflower	T-Mulz A02	1.3	1.8	2.8	2.0
Sunflower	Triton® X-45	1.0	1.0	2.7	1.6
Methylated sun	None	1.2	5.0	5.0	3.7
Methylated sun	Atplus 300F	2.3	5.0	5.0	4.1
Methylated sun	T-Mulz A02	1.2	4.5	4.8	3.5
Methylated sun	Triton® X-45	1.3	5.0	5.0	3.8

Note: Evaluation scale: 1.0, no solubility; 3.0, smeared circle where oil droplet was placed; 5.0, clear circle where oil droplet was placed; 7.0, smeared oblong where oil droplet was placed and drained off; 9.0, clear oblong where oil droplet was placed and drained off.

LSD, 0.05; oil by emulsifier and time, 0.5; oil by emulsifier, 0.3.



TABLE 4  
Green Foxtail Injury and Electroconductivity of  
Incubation Solution Containing Leaf Disks  
Treated with Once-Refined and Alkane Esters  
of Vegetable Oil

Ester	Crop origin*					
	Injury (%)			Electroconductivity ( $\mu$ mhos/cm)		
	Lin	Cot	Sun	Lin	Cot	Sun
Triglyceride	1	1	0	2	2	2
Methyl	27	41	35	47	86	60
Ethyl	28	13	5	24	10	12
Butyl	25	4	3	28	5	9

Note: LSD, 0.05; injury, 11; electroconductivity, 15.

\* Lin, linseed oil; cot, cottonseed oil; sun, sunflower oil.

oil may affect emulsion stability, spray droplet retention and spreading, and/or directly affect foliar absorption of the pesticide.

#### B. LEAF-CELL MEMBRANE PERMEABILITY

The electroconductivity of the solution in which leaf disks treated with oil were incubated was used to measure the effect of the oils on leaf-cell membrane permeability. The assumption was that the electroconductivity of the incubation solution would increase with leaf-cell membrane permeability.

Oils did not affect green foxtail leaf-cell membrane permeability after 2.5 or 60 min, but did 24 h after treatment; thus, the data presented in Table 4 are only for the 24-h rating. Electrolyte leakage from leaf disks was greater when treated with methyl-esterified vegetable oils than when treated with butyl- or ethyl-esterified, or once-refined vegetable oils (Table 4). Crop origin affected the electrolyte leakage from leaf disks treated with methyl-, ethyl-, or butyl-esterified vegetable oil, but not with once-refined vegetable oil. Methylated cottonseed oil caused greater leakage than methylated linseed or methylated sunflower oil. Triglycerides, and the ethyl and butyl esters of cottonseed and sunflower oil, caused similar electrolyte leakage from the green foxtail leaf disks, and this leakage was not significantly greater than electrolyte leakage from untreated leaf disks. However, electrolyte leakage was greater from leaf disks treated with ethyl or butyl esters of linseed oil than from leaf disks treated with once-refined linseed oil or untreated leaf disks.

The electrolyte leakage from leaf disks treated with esterified vegetable oils did not correlate with the relative wax solubility of the esterified vegetable oils. The methyl-, ethyl-, and butyl-esterified fatty acids had similar relative wax solubility values, but differed in their effect on leaf-cell membrane permeability (Tables 2 and 4).

Methyl-, ethyl-, and butyl-esterified vegetable oils injured green foxtail slightly to moderately, whereas the triglycerides (once-refined vegetable oils) did not injure them 24 h after treatment (Table 4). Methyl-esterified vegetable oils, except linseed oil, caused greater injury than ethyl- or butyl-esterified vegetable oils. Linseed oil free fatty acid methyl, ethyl, and butyl esters all equally injured green foxtail. Green foxtail injury was greater from the ethyl and butyl esters of linseed oil than from those of cottonseed or sunflower oils. Green foxtail was injured more by methylated cottonseed oil than by any of the other oils.



Triglycerides (vegetable oils) had low relative wax solubility, did not affect cell membrane permeability, and did not cause leaf injury to green foxtail. Methyl-, ethyl-, and butyl-esterified vegetable oils had similar relative wax solubilities, which were greater than that of vegetable oil. Methyl-esterified vegetable oils generally caused greater cell membrane permeability and leaf injury than ethyl- or butyl-esterified vegetable oils.

The characteristics of an oil responsible for the greater cell membrane leakage and leaf injury from methyl- than from ethyl- or butyl-esterified fatty acids are not known. Perhaps methyl esters with greater polarity or smaller molecular size are better able than ethyl or butyl esters to cross the cell wall and/or disrupt the cell membrane. Esterases in the leaf may catalyze the cleaving of the ester bond, releasing a free fatty acid and alcohol. Perhaps these esterases are more capable of cleaving methyl esters than ethyl or butyl esters of fatty acids and the free fatty acid is causing the injury and/or the methanol is more phytotoxic than ethanol or butanol. Free fatty acids are more phytotoxic than the alkane esters of fatty acids (unpublished data).

The effect of esterified fatty acids on leaf-cell membrane permeability and leaf injury does not seem to relate to the effectiveness of these oils as spray adjuvants. Esterified vegetable oil fatty acids were equally as, and often more effective than, once-refined vegetable oil in enhancing herbicide phytotoxicity.<sup>9</sup> Field experiments have indicated no differences among methyl, ethyl, or butyl esters of vegetable oil as spray adjuvants for herbicides (Manthey et al., unpublished data). The relative wax solubility values for methyl-, ethyl-, and butyl-esterified vegetable oil fatty acids were similar and were greater than once-refined vegetable oil. Thus, relative wax solubility of an oil in leaf wax may relate to the effectiveness of an oil in enhancing herbicide efficacy.

Petroleum oil and sunflower oil alone or with emulsifier did not affect cell membrane permeability compared to distilled water 2.5 min, 60 min, or 24 h after treatment (Table 5). Methylated sunflower oil containing 15% (v/v) Triton X-45 caused more electrolyte leakage than methylated sunflower oil alone or with 15% (v/v) Atplus 300F 60 min after treatment. Further, methylated sunflower oil containing T-Mulz A02 or Triton X-45 caused more electrolyte leakage than methylated sunflower oil alone or with Atplus 300F 24 h after treatment. Leakage from methylated sunflower oil-treated leaves was greatest with Triton X-45, intermediate with T-Mulz A02, and least with Atplus 300F, when averaged over time.

Green foxtail was injured more by methylated sunflower oil with or without emulsifier than by distilled water, petroleum oil, or sunflower oil with or without an emulsifier (Table 5). Green foxtail injury was greater when treated with an oil containing either T-Mulz A02 or Triton® X-45 than with an oil containing Atplus 300F or no emulsifier, averaged over oils. The phytotoxicity of an emulsifier-oil carrier or adjuvant seems dependent upon both the emulsifier and the oil. The emulsifier could be phytotoxic and the oil could facilitate the passage of the emulsifier across the cuticle and/or the oil could be phytotoxic and the emulsifier could facilitate the passage of the oil across the cell wall. Some green foxtail injury occurred with treatments of petroleum and sunflower oil without detectable electrolyte leakage. Thus, electrolyte leakage does not always occur or is not detectable when injury is slight. Previous research indicated that electrolyte leakage from cells did not always occur with injury.<sup>12</sup>

Oils differed in their relative solubility in green foxtail leaf wax, their effect on leaf-cell membrane permeability, and their phytotoxicity. Emulsifiers differed in their influence on the solubility of the oils in leaf wax, effect on leaf-cell membrane permeability, and phytotoxicity. Information concerning the relative solubility of oils and oils with emulsifiers in leaf wax, and the effect of oils alone and with an emulsifier on leaf-cell membrane permeability and phytotoxicity, may be useful in selecting oils and emulsifiers as pesticide formulants, spray adjuvants, and spray carriers.

TABLE 5  
Leaf Cell Permeability from Oils as Influenced by Emulsifier  
and Time

Oil <sup>b</sup>	Emulsifier	Electroconductivity (μmhos) <sup>a</sup>				
		Time (min)			Mean	Injury (%, 24 h) <sup>c</sup>
		2.5	60	1440		
Distilled water	None	23	21	23	23	0
	Atplus 300F	23	23	24	23	0
	T-Mulz A02	24	24	26	25	0
	Triton X-45	22	23	23	22	1
POIIN	None	23	24	24	24	4
	Atplus 300F	22	23	24	23	4
	T-Mulz A02	22	25	30	26	14
	Titron X-45	22	23	23	23	6
Sunflower (sun)	None	22	22	23	23	10
	Atplus 300F	23	22	23	23	11
	T-Mulz A02	24	22	23	23	15
	Triton X-45	24	23	26	24	21
Methylated sun	None	25	31	87	48	52
	Atplus 300F	25	31	95	50	51
	T-Mulz A02	28	38	106	57	55
	Triton® X-45	27	46	147	74	59

Note: LSD (0.05).

<sup>a</sup> Oil by emulsifier by time, 12; oil by emulsifier, 7.

<sup>b</sup> Oil-emulsifier combinations applied as spray carriers contained 15% (v/v) emulsifier. Distilled water-emulsifier combinations applied as spray carriers contained 1.5% (v/v) emulsifier.

<sup>c</sup> Oil by emulsifier, NS; emulsifier, 4; oil, 4; RCBD, 9.

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## Chapter 45

**PHYTOTOXICITY OF BENTAZON WITH OILS, SURFACTANTS,  
AND FERTILIZER SALTS**

Frank A. Manthey, Edward F. Szelezniak, and John D. Nalewaja

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## ABSTRACT

Experiments were conducted to determine the effect of oils, surfactants, and fertilizer salts on bentazon toxicity to *Amaranthus retroflexus* L. (redroot pigweed), *Chenopodium album* L. (common lambsquarters), and *Kochia scoparia* (L.) Schrad. (kochia). Adjuvant enhancement of bentazon phytotoxicity depended upon plant species. In greenhouse experiments, oil and surfactant adjuvants were equally as or more effective than oil/surfactant-fertilizer salt combinations or fertilizer salts in enhancing bentazon toxicity to *A. retroflexus*. However, certain oil/surfactant-fertilizer salt combinations were more effective than oils, surfactants, or fertilizer salts in enhancing bentazon toxicity to *C. album* and *K. scoparia*. In field experiments, oils were more than or equally as effective as oil-fertilizer salt combinations or fertilizer salts in enhancing bentazon toxicity to *A. retroflexus*, *C. album*, and *K. scoparia*. *Glycine max* (L.) Merr. (soybeans) was not injured by bentazon applied with various oil-fertilizer salt combinations in the field. Scanning electron microscopy micrographs indicated that *C. album* and *K. scoparia* had a similar crystalline wax structure on their adaxial leaf surface, while *A. retroflexus* epicuticular wax appeared to be amorphous. Differences in leaf surface morphology may help explain why *A. retroflexus* responded differently than *C. album* and *K. scoparia* to bentazon applied with various adjuvants.

## I. INTRODUCTION

Bentazon, [3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide] is a postemergence herbicide for selective control of broadleaf weeds in *G. max*. Bentazon inhibits the photosynthetic electron transport system, which results in free radical formation. The free radicals destroy the plasma membrane, which results in cell death.<sup>17</sup> Differential tolerance between tolerant and susceptible species to bentazon generally is related to bentazon metabolism and not to differences in absorption and translocation.<sup>3,4,10</sup> Tolerant species metabolize bentazon more rapidly than susceptible species. Differential tolerance between susceptible species may be due to differences in bentazon absorption.<sup>12</sup>

Fertilizer salts, surfactants, and oils have enhanced bentazon phytotoxicity.<sup>11,13,15,19</sup> This enhancement is probably due to the increase rate and total amount of bentazon absorbed,<sup>12,19</sup> which overwhelms the plant's ability to detoxify bentazon.

Leaf surface morphology differs with plant species.<sup>1</sup> The wettability and retention of foliar sprays depend on the surface morphology and nature of the chemical groups of the wax exposed at the surface.<sup>7,16</sup> This may partially explain why plant species differ in their response to adjuvants applied with bentazon.<sup>5,6,15</sup>

The objective of this research was to determine the toxicity of bentazon to *A. retroflexus*, *C. album*, and *K. scoparia* as influenced by various oils, surfactants, and fertilizer salts.

## II. MATERIALS AND METHODS

## A. GREENHOUSE EXPERIMENTS

*A. retroflexus*, *C. album*, and *K. scoparia* were grown in soil contained in 0.5-l plastic pots. *A. retroflexus* was thinned to seven, *C. album* to ten, and *K. scoparia* to ten plants per pot 1 week after emergence. The soil was watered daily as needed. The natural-day length was supplemented using metal halide lamps, providing the plant area with an intensity of  $450 \mu\text{E m}^{-2} \text{s}^{-1}$  for a 16-h photoperiod. The soil surface was covered with vermiculite prior to and removed after treatment to prevent root absorption of the bentazon. Treatments were applied to four-leaf *A. retroflexus*, four- to six-leaf *C. album*, and five- to six-cm-tall *K. scoparia*. Treatments were applied with a moving nozzle pot sprayer delivering 160



l/ha at 275 kPa air pressure. Shoot fresh weight per pot was determined 14 d after treatment, and data were expressed as the percentage weight reduction compared to untreated control plants.

The contact angle of the spray solution was determined using a microp projector. Light was directed across a fresh leaf attached to a microscope slide. A 10- $\mu$ l droplet was placed on the adaxial leaf surface. The magnified image was projected and traced onto paper. Contact angles were determined from the tracings, using a protractor. Tracings were made within 15 s after droplet placement. Six droplets were traced per treatment.

Wax deposits on the adaxial leaf surface of *A. retroflexus*, *C. album*, and *K. scoparia* were examined by scanning electron microscopy (SEM) at the Electron Microscopy Laboratory, Northern Crop Sciences Laboratory, North Dakota State University, Fargo. Samples were prepared for low-temperature SEM using an EM SCOPE 2000A cryo unit. Samples were frozen in liquid nitrogen slush, sublimed for 8 min at  $-60^{\circ}\text{C}$ , sputter coated with gold, and examined in a JEOL JSM-35 scanning electron microscope at  $-176^{\circ}\text{C}$ .

### 1. Surfactants

Bentazon was applied at 0.42 kg of active ingredient (a.i.) per ha to *A. retroflexus* and 0.56 kg/ha to *K. scoparia*. Surfactants were applied at 0.25% (v/v) of the spray volume. A petroleum oil containing 15% (v/v) Atplus<sup>®</sup> 300F emulsifier was applied at 2.3 l/ha. Each plant species was a separate experiment. The experimental design was a randomized complete block with five replications. Each experiment was repeated once in time.

### 2. Fertilizer Salts

Bentazon was applied at 0.42 kg a.i./ha to *A. retroflexus* and 0.56 kg/ha to *K. scoparia*. Fertilizer salts were analytical grade and were applied at 4.5 kg/ha, and aqueous 28-0-0, which consisted of equal parts of urea and ammonium nitrate, was applied at 9.4 l/ha. A petroleum oil containing 15% (v/v) Atplus 300F emulsifier was applied at 2.3 l/ha. Each plant species was a separate experiment. The experimental design was a randomized complete block with five replications. Each experiment was repeated once in time.

### 3. Oil/Surfactant by Fertilizer Salts

Bentazon was applied at 0.42 kg a.i./ha to *A. retroflexus*, 0.18 kg/ha to *C. album*, and 0.28 kg/ha to *K. scoparia*. Oils containing 15% (v/v) Atplus 300F emulsifier were applied at 2.3 l/ha, surfactants were applied at 0.25% (v/v) of the spray volume, and fertilizer salts were applied at 4.5 kg/ha. Each plant species was a separate experiment. The experimental design was a randomized complete block with a factorial arrangement of oil surfactant and fertilizer salts and had five replications. Each experiment was repeated once in time.

## B. FIELD EXPERIMENTS

Field treatments were applied using a bicycle wheel plot sprayer delivering 80 l/ha at 275 kPa air pressure. Treatments were applied to "McCall" *G. max* in the first trifoliolate leaf stage and 5- to 10-cm-tall *C. album* and *K. scoparia* at Prosper, ND, and to McCall *G. max* in the third trifoliolate leaf stage, four- to six-leaf *A. retroflexus*, and 5- to 7-cm-tall *K. scoparia* at Fargo, ND. Bentazon was applied at 0.7 kg/ha. Oils containing 15% (v/v) Atplus 300F emulsifier were applied at 2.3 l/ha. Fertilizer salts were applied at 2.8 kg/ha, and aqueous 28-0-0 was applied at 9.4 l/ha. Visible injury ratings were determined 2 weeks after treatment using a scale of 0 (no injury) to 100 (complete kill). Each species was analyzed separately, and data for *G. max* and *K. scoparia* were combined over locations. The experimental design was a randomized complete block with a factorial arrangement of oil and fertilizer salts and had four replications.

TABLE 1  
Fresh Weight Reduction of *A. retroflexus* and *K. scoparia* by  
Bentazon and Spray Droplet Contact Angle on *K. scoparia* Leaf as  
Influenced by Surfactants

Surfactant	Fresh wt reduction(%)		Contact angle(°) <i>K. scoparia</i>
	<i>Amaranthus retroflexus</i>	<i>Kochia scoparia</i>	
None	78	6	135
Atplus 300F	84	71	98
Du Pont Spreader/Sticker	86	93	70
Du Pont WK	96	97	6
Emulsifier X-363	88	89	9
Igepal CO-430	87	90	23
Igepal CO-610	88	84	8
Igepal CO-630	88	78	72
Tergitol 15-S-5	83	95	10
T-Mulz VO	89	84	64
Triton X-100	90	79	66
X-77	88	89	13
Petroleum oil	88	81	92
LSD (0.05)	5	9	10

Note: Bentazon was applied at 0.42 kg a.i./ha to *A. retroflexus* and at 0.52 kg/ha to *K. scoparia*. Surfactants were applied at 0.25% (v/v) of 160 l/ha spray volume. Petroleum oil contained 15% (v/v) Atplus 300F emulsifier and was applied at 2.3 l/ha. LSD, least significant difference.

### III. RESULTS AND DISCUSSION

#### A. GREENHOUSE EXPERIMENTS

##### 1: Surfactants

Bentazon was more toxic to *A. retroflexus* and *K. scoparia* when applied with than without a surfactant (Table 1). *A. retroflexus* fresh weight reduction was greatest when bentazon was applied with DuPont® WK and least when applied with Atplus 300F or Tergitol 15-S-5. *K. scoparia* fresh weight reduction was greater when bentazon was applied with DuPont Spreader/Sticker, DuPont WK, Igepal® CO-430, Tergitol 15-S-5, or X-77 than when applied with Atplus 300F, Igepal CO-630, or Triton® X-100. Atplus 300F was the least effective surfactant and DuPont WK was the most effective surfactant for bentazon toxicity to *A. retroflexus* and *K. scoparia*. Tergitol 15-S-5 was one of the best surfactants for *K. scoparia*, but one of the least effective surfactants for *A. retroflexus*. Thus, the effectiveness of a surfactant in enhancing bentazon phytotoxicity depends on plant species. Surfactants have differed in their effectiveness in enhancing herbicide phytotoxicity, and their effectiveness has been shown to be species dependent.<sup>8,15</sup>

The leaf surface morphology among plant species is very diverse.<sup>1</sup> SEM micrographs of the adaxial leaf surface of *A. retroflexus* and *K. scoparia* show that *K. scoparia* leaves have a crystalline wax formation, while the wax on *A. retroflexus* leaves appears amorphous (Figure 1). The difference in leaf surface wax morphology between *A. retroflexus* and *K. scoparia* may help explain the differences in surfactant efficacy with bentazon for these two plant species.

Spray droplet contact angle gives a measure of leaf wettability by the spray mixture. A high contact angle indicates low wettability, while a low contact angle indicates high wet-

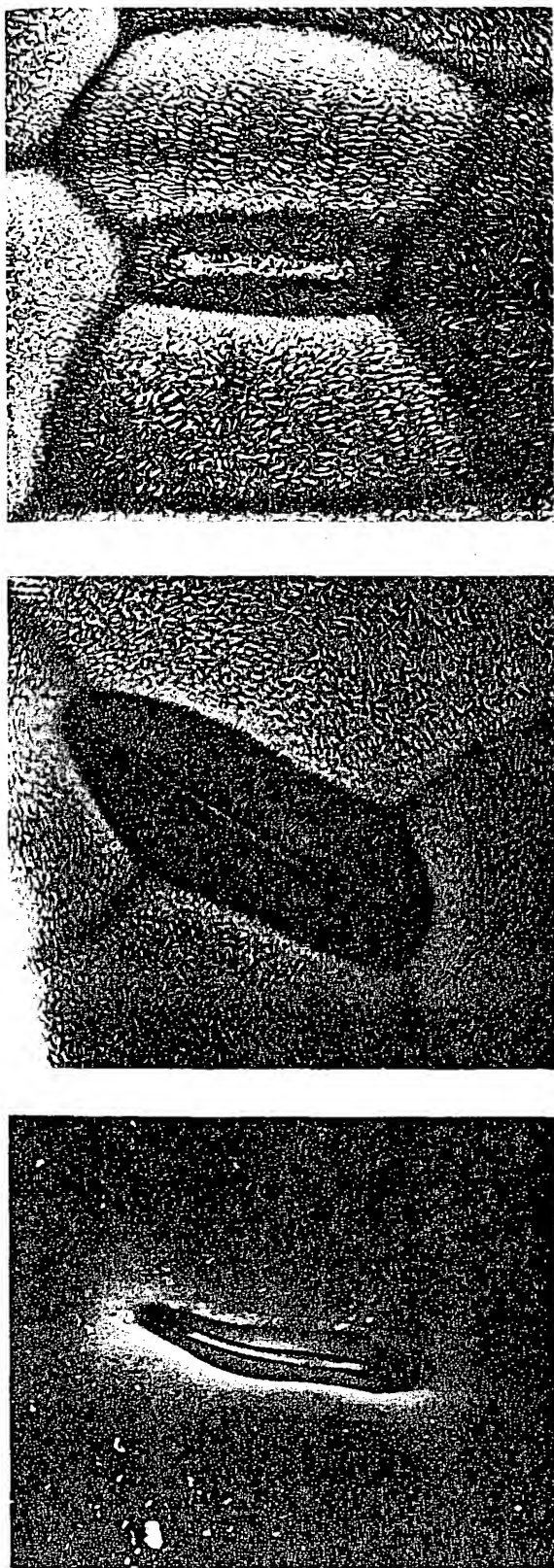


FIGURE 1. SEM micrographs of adaxial leaf surfaces of (A) *A. retroflexus*; (B) *C. album*; and (C) *K. scoparia*. (Magnification  $\times 2400$ .)

TABLE 2  
Fresh Weight Reduction of *A. retroflexus* and *K. scoparia* by  
Bentazon and Spray Droplet Contact Angle on *K. scoparia*  
Leaf as Influenced by Fertilizer Salts

Fertilizer salt	Fresh wt reduction (%)		Contact angle (°)
	<i>Amaranthus retroflexus</i>	<i>Kochia scoparia</i>	
None	79	29	135
Ammonium nitrate	81	78	137
Ammonium sulfate	73	51	142
Calcium chloride	82	—	—
Calcium nitrate	77	17	133
Magnesium sulfate	82	—	—
Potassium nitrate	86	70	135
Potassium phosphate	87	68	—
Sodium chloride	68	56	135
Urea	83	37	137
UAN	83	67	133
Zinc sulfate	58	—	—
Petroleum oil	91	96	100
LSD (0.05)	10	9	8

Note: Bentazon was applied at 0.42 kg a.i./ha to *A. retroflexus* and at 0.56 kg/ha to *K. scoparia*. Fertilizer salts were applied at 4.5 kg/ha. Potassium phosphate was monobasic. UAN is an aqueous solution containing equal amounts of urea and ammonium nitrate which provides 28% nitrogen. Petroleum oil contained 15% (v/v) Atplus 300F emulsifier and was applied at 2.3 l/ha. LSD, least significant difference.

tability. The contact angle of the spray droplet seemed to relate to the effectiveness of the surfactant in enhancing bentazon toxicity to *K. scoparia* (Table 1). The best surfactants generally resulted in low spray droplet contact angles (6 to 23).

Contact angle alone cannot explain surfactant efficacy. Du Pont Spreader/Sticker was quite effective in enhancing bentazon toxicity to *K. scoparia*, and the spray droplet had a contact angle of 70. Igepal CO-630 and Triton X-100 were less effective than Du Pont Spreader/Sticker in enhancing bentazon toxicity to *K. scoparia*, yet all three surfactants resulted in similar spray droplet contact angles on *K. scoparia* leaves. Surfactants, in addition to lowering spray droplet contact angle, may enhance herbicide phytotoxicity by increased wetting of the plant foliage,<sup>16</sup> solubilization of the active ingredient,<sup>18</sup> and/or disruption of the epicuticular wax.<sup>9</sup>

## 2. Fertilizer Salts

Fertilizer salts did not significantly enhance bentazon toxicity to *A. retroflexus* (Table 2). Potassium nitrate and potassium phosphate were similar to petroleum oil in enhancing bentazon toxicity to *A. retroflexus*. Sodium chloride and zinc sulfate reduced bentazon phytotoxicity to *A. retroflexus* compared to bentazon applied alone.

Petroleum oil was more effective than fertilizer salts in increasing bentazon toxicity to *K. scoparia*. Of the fertilizer salts tested, ammonium nitrate generally resulted in the best bentazon enhancement of *K. scoparia* fresh weight reduction. Urea had no effect and calcium nitrate reduced bentazon toxicity to *K. scoparia*. Thus, the effectiveness of these fertilizer salts in enhancing bentazon phytotoxicity depended on the fertilizer salt and plant species. Fertilizer salts differed in their effect on the phytotoxicity of bentazon,<sup>19</sup> glyphosate,<sup>20</sup> picloram,<sup>21</sup> and sethoxydim.<sup>2</sup>



Fertilizer salts may increase herbicide phytotoxicity by increasing the rate or period of herbicide absorption. How fertilizer salts function in enhancing herbicide absorption is not well understood. Fertilizer salts may modify herbicide phytotoxicity by interacting with surfactants or with the ions present in commercially formulated herbicides.<sup>20</sup> Certain fertilizer salts may affect herbicide activity by interacting with the macromolecules which constitute various plant membranes in ways analogous to the "salting in" and "salting out" of proteins.<sup>14,20</sup>

The effect of fertilizer salt on spray droplet contact angle did not relate to salt effectiveness, suggesting that salts have a function other than increasing the wettability of the spray solution on the leaf surface (Table 2).

### 3. Oil/Surfactant by Fertilizer Salts

The oil/surfactant by fertilizer salt interaction was significant for *A. retroflexus*, *C. album*, and *K. scoparia* (Table 3). The effect of a particular oil/surfactant-fertilizer salt combination on bentazon phytotoxicity depended on the oil or surfactant and fertilizer salt.

The toxicity to *A. retroflexus* by bentazon applied with an oil or surfactant was not enhanced or was reduced by the inclusion of a fertilizer salt in the spray solution (Table 3). Conversely, *A. retroflexus* fresh weight reduction by bentazon applied with ammonium nitrate was not increased by the inclusion of a surfactant or oil in the spray solution. *A. retroflexus* fresh weight reduction was greater when bentazon was applied with petroleum oil than with any other oil or surfactant, fertilizer salt, or oil/surfactant-fertilizer salt combination. Thus, there was no advantage and often a disadvantage in using an oil-surfactant-fertilizer salt blend compared to using only an oil or surfactant for *A. retroflexus* control with bentazon.

The toxicity of bentazon to *C. album* and *K. scoparia* was greater with bentazon applied with oil/surfactant-fertilizer salt combinations compared to bentazon applied with fertilizer salts (Table 3). The toxicity of bentazon applied with Atplus 300F or petroleum oil was enhanced by the inclusion of fertilizer salts in the spray solution. However, the toxicity of bentazon applied with methylated sunflower oil or sodium salt of sunflower oil free fatty acids to *C. album* and *K. scoparia* was not affected or was reduced by the inclusion of fertilizer salts in the spray solution. These data indicate that combinations of oil/surfactant-fertilizer salt are not always more effective than an oil or surfactant in enhancing bentazon toxicity to *C. album* and *K. scoparia*.

Species differed in their response to bentazon applied with an oil, surfactant, fertilizer salt, or an oil surfactant-fertilizer salt combination (Table 3). Atplus 300F, sunflower oil, or petroleum oil combined with fertilizer salts were equally as, or more effective than the oil, surfactant, or fertilizer salts applied alone in enhancing bentazon toxicity to *C. album* and *K. scoparia*. However, the oil/surfactant-fertilizer salt combinations were all equally as, or less effective than oil or surfactant in enhancing bentazon toxicity to *A. retroflexus*.

## B. FIELD EXPERIMENTS

Bentazon applied alone or with any of the various oil-fertilizer salt combinations caused less than 5% injury to *G. max* 2 weeks after treatment (data not presented).

Surfactant X-77 was less effective than petroleum oil in enhancing *C. album* and *K. scoparia* control with bentazon, but was as effective as petroleum oil in enhancing *A. retroflexus* control with bentazon (data not presented).

Oil adjuvants enhanced bentazon toxicity to *C. album* and *K. scoparia* more than to *A. retroflexus* (Table 4). Bentazon applied with an oil adjuvant gave similar control of all three species. Petroleum oil and methylated sunflower oil caused a greater enhancement of bentazon toxicity to *C. album* and *K. scoparia* than to *A. retroflexus*. For example, control of



TABLE 3  
Fresh Weight Reduction of *A. retroflexus*, *C. album*, and *K. scoparia* by Bentazon  
as Influenced by Oil/Surfactant and Fertilizer Salt Combinations in the  
Greenhouse

Oil/surfactant	Fertilizer salts (% fresh wt reduction)			
	None	Ammonium sulfate	Ammonium nitrate	Potassium nitrate
<i>A. retroflexus</i> <sup>a</sup>				
None	57	51	76	70
DuPont WK	79	82	74	83
Atplus 300F	82	77	69	84
Sunflower	74	62	63	79
Methylated sunflower	70	64	53	66
Sodium salt sunflower	80	53	64	77
Petroleum	94	79	77	92
<i>C. album</i> <sup>b</sup>				
None	10	1	11	8
DuPont WK	79	74	67	62
Atplus 300F	13	48	40	22
Sunflower	39	49	43	39
Methylated sunflower	39	29	39	43
Sodium salt sunflower	52	26	23	40
Petroleum	22	55	55	48
<i>K. scoparia</i> <sup>c</sup>				
None	5	17	30	25
DuPont WK	97	98	98	90
Atplus 300F	66	87	94	73
Sunflower	85	88	91	82
Methylated sunflower	91	89	90	90
Sodium salt sunflower	84	80	80	90
Petroleum	90	96	96	94

Note: Fertilizer salts were applied at 2.8 kg/ha. Surfactants were applied at 0.25% (v/v) spray volume, oils contained 15% (v/v) Atplus 300F emulsifier and were applied at 2.3 l/ha.

<sup>a</sup> Bentazon applied at 0.42 kg/ha; LSD (0.05): oil by salt, 7; salt, 2; oil, 3.

<sup>b</sup> Bentazon applied at 0.18 kg a.i./ha; LSD (0.05): oil by salt, 8; salt, not significant; oil, 4.

<sup>c</sup> Bentazon applied at 0.28 kg/ha; LSD (0.05): oil by salt, 6; salt, 2; oil, 3.

*A. retroflexus*, *C. album*, and *K. scoparia* was 18, 58, and 56% greater, respectively, when bentazon was applied with methylated sunflower oil adjuvant than when applied without an adjuvant. Fertilizer salts caused little enhancement of bentazon phytotoxicity in the field. Oil-fertilizer salt combinations were less or equally as effective as the oils alone in enhancing the control of *A. retroflexus*, *C. album*, and *K. scoparia* by bentazon. Thus, there was no additional benefit from the inclusion of a fertilizer salt in the spray solution containing bentazon and an oil adjuvant for *A. retroflexus*, *C. album*, and *K. scoparia* control.

Petroleum oil and methylated sunflower oil similarly enhanced bentazon toxicity to *A. retroflexus*, *C. album*, and *K. scoparia* (Table 4). Although petroleum oil tended to be more effective than methylated sunflower oil in enhancing bentazon toxicity to *C. album* and *K. scoparia*, results from field experiments from previous years have indicated that methylated sunflower oil was as effective as petroleum oil in enhancing bentazon phytotoxicity (Manthey

TABLE 4  
Injury of *A. retroflexus*, *C. album*, and *K. scoparia*  
by Bentazon as Influenced by Oil and Fertilizer  
Salt Combinations in the Field

Fertilizer salts	Oils (% control)			Mean
	None	Petroleum	MSF	
<i>A. retroflexus</i> <sup>a</sup>				
None	56	76	74	69
Ammonium sulfate	52	73	71	65
Ammonium nitrate	45	70	60	58
UAN	51	69	61	61
Potassium nitrate	67	77	68	71
Sodium bicarbonate	67	79	79	75
Mean	56	74	69	—
<i>C. album</i> <sup>b</sup>				
None	14	84	72	57
Ammonium sulfate	20	82	78	60
Ammonium nitrate	19	82	68	56
UAN	19	74	60	51
Potassium nitrate	19	73	70	54
Sodium bicarbonate	33	83	60	58
Mean	21	80	68	—
<i>K. scoparia</i> <sup>c</sup>				
None	14	82	70	56
Ammonium sulfate	26	79	84	63
Ammonium nitrate	17	84	73	58
UAN	32	77	73	61
Potassium nitrate	28	77	63	56
Sodium bicarbonate	24	78	68	57
Mean	24	80	72	—

Note: Bentazon was applied at 0.7 kg a.i./ha. Petroleum oil and methylated sunflower oil (MSF) contained 15% (v/v) Atplus 300F emulsifier and were applied at 2.3 l/ha. Fertilizer salts were applied at 2.8 kg/ha. UAN is an aqueous solution containing equal amounts of urea and ammonium nitrate which provides 28% nitrogen.

<sup>a</sup> LSD (0.05): salt by oil, not significant (NS); oil, 5; salt, 7; RCBD, 12.

<sup>b</sup> LSD (0.05): salt by oil, NS; oil, 7; salt, NS; RCBD, 16.

<sup>c</sup> LSD (0.05): salt by oil, NS; oil, 6; salt, NS; RCBD, 14.

et al., unpublished data). Further, methylated sunflower oil was as effective as petroleum oil in enhancing bentazon toxicity to *K. scoparia*, and more effective than petroleum oil in enhancing bentazon toxicity to *C. album* in greenhouse experiments (Table 3). Petroleum oil has been as effective as methylated sunflower oil in enhancing bentazon toxicity to *C. album* in other greenhouse experiments. Thus, petroleum oil and methylated sunflower oil

probably are equally effective in enhancing bentazon toxicity to *A. retroflexus*, *C. album*, and *K. scoparia*.

The greenhouse and field results indicate that *C. album* and *K. scoparia* respond differently than *A. retroflexus* to bentazon applied with oil-fertilizer salt combinations (Tables 3 and 4). *C. album* and *K. scoparia* have a crystalline wax structure on their leaf surfaces and *A. retroflexus* leaf surface wax appears to be amorphous (Figure 1). This may explain the similar response of *C. album* and *K. scoparia* compared to the response of *A. retroflexus* to the oil/surfactant/fertilizer salt combinations with bentazon.

These data indicate that the most effective adjuvant for bentazon depends on the plant species. Spray adjuvant-herbicide efficacy relationships are very complex. Fertilizer salts in spray solution containing bentazon and an oil or surfactant increased, decreased, or had no effect on bentazon phytotoxicity, depending on the fertilizer salt, surfactant or oil, and plant species. However, surfactants and oils were generally more effective than fertilizer salts in enhancing bentazon phytotoxicity. *A. retroflexus*, *C. album*, and *K. scoparia* can be found growing in the same field. The best adjuvant to use for a mixture of plant species will be one that provides a satisfactory level of bentazon toxicity to all the weed species present. The information on the influence of specific oil, surfactant, and fertilizer salt adjuvants on bentazon control of various weed species provides a base for the development of adjuvants for bentazon to control specific or a combination of weed species.

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### *Section III*

Rationale for Use; Concerns within the Pesticide Industry; Evaluation  
Methodology; Efficacy with Herbicides and Growth Regulators;  
Enhancement of Disease and Insect Control

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## Chapter 46

**THE RATIONALE FOR ADJUVANT USE WITH  
AGRICHEMICALS**

B. G. Reeves

**I. THE RATIONALE FOR ADJUVANT USE WITH  
AGRICHEMICALS**

Undoubtedly there does not exist any dispute over the basic premise that the world's agricultural production will need to expand dramatically in the future. The quantity as well as the quality will have to increase in the following areas: food for humans, food for livestock as well as fiber, and other agriculturally produced building materials. Most likely this increased production will see a proportionate increase in demands on pesticides as well as other agrichemical products.

We have all read or heard of the dire predictions of the 19th century economist, Thomas Malthus, who in 1798 published "An Essay on the Principle of Population". In short, Malthus indicated the population of the earth would grow faster than our ability to produce food necessary to feed that population. A quick review of the numbers indicates that Malthus was certainly correct in his assessment of the human ability to populate this planet. World population figures show that since 1930, when we had a mere 2 billion, we have indeed grown rapidly — to 3 billion in 1960, nearly 4 billion in 1976, and 5 billion people in 1988. At these rates, there will most likely be 6.5 billion inhabitants on earth by the turn of the century. Many others today disagree with the Malthusian proposal including the author of this chapter. While his concept that Earth's resources are finite and therefore have a limited capacity to produce is technically correct, Malthus certainly overlooked or underestimated two important factors: human ingenuity and improving technological capabilities.

If future demands are to be met, changes will surely be necessary. Some of the changes have already started that will help us meet the challenges of the future. Perhaps the most important key to increasing agricultural production is to be found in production efficiency. Specifically, it will be our ability to improve efficiency in all aspects and levels of production agriculture that will determine success in meeting the challenge of the future.

All aspects, including seed selection, planting, fertilization, crop protection chemicals, cultural practices, irrigation, harvest, transportation, storage, and processing will have to be examined from the perspective of improving efficiency. It has been estimated that from planting to consumption, over 50% of the world's production of food is lost to weeds, pests, and diseases, as well as other contributing factors. Clearly, much room exists for improvement. Technology will certainly provide the means by which new products and methods will meet the demands described previously. Technology will likewise improve old materials and processes to make them more appropriate for future use. The new products will be produced by both conventional and biotechnological means. Most likely, as it has been in the past, it will be a combination of the new and the old that will contribute to the overall effort of production.

In summary, there are two approaches to the problem of increased production. First, yield per unit could be improved and the number of producing units expanded. Second, losses could be prevented or minimized.

Among the agrichemical products available to producers is a little known, little understood group of materials called adjuvants, which assist the performance of the basic pesticidal or chemical products. To define the manner in which adjuvant products exhibit their utility,

a basic outline form will be employed. The outline is based on the premise that, in the broadest sense, there are but three reasons to use adjuvant materials.

1. **To improve or otherwise facilitate the physical handling characteristics of agri-chemicals.** This can be considered in two phases. The first being the consideration of those situations that can arise during the mixing and any subsequent storage of the spray solution. During this phase, problems with foaming, incompatibility, or suspension can and do occur. There are specific adjuvant products designed to assist with each of these situations. The other aspect concerns the spray and mixing equipment. The major concern seems to be with residue that is left in the equipment and may be potentially injurious to crops in subsequent applications. Additionally, staining by chemicals may obscure sight gauges and also cause a general adverse appearance problem.
2. **To improve performance effectiveness and consistency.** The ability of adjuvant materials to impact this area is perhaps the most important reason that they are used. At the risk of oversimplification, it appears that there are only two routes by which performance can be affected with adjuvant usage. First is the minimization of chemical loss and second, the maximization of the agrichemical's effect once it is placed on the target. To understand how adjuvants may minimize chemical losses, one must first know the major contributors to those losses. The main ones are drift, in-flight evaporation, in-flight volatilization, droplet shatter, bounce or runoff, washoff, and removal by wind or plant growth. These losses result in agrichemicals never reaching the target or achieving only a transitory deposit. Adjuvant materials have been designed to modify spray droplet characteristics to minimize these kinds of losses. Other types of chemical losses can be compensated for with the use of adjuvant products. These losses are chemical degradation (hydrolysis) due to alkaline spray solutions and the "natural" forces of environment which break down agrichemicals. Hydrolysis is an action that usually takes place in the spray or mix tank, while the "natural" forces are those that happen after the agrichemical is placed on the target. Extremes in environmental conditions (heat, light, and moisture) can accelerate the breakdown beyond normal rates. Maximizing the effect of agrichemicals once delivered to the target can also be seriously affected by adjuvants. There are three basic methods for achieving an enhanced effect. The first is to improve coverage of the spray solution, which can be accomplished by lowering the surface tension of the spray with surfactant materials. The second is by improving the penetration or uptake into the target pest. This becomes important with herbicides, systemic fungicides and insecticides, growth regulators, and nutrients. Special types of adjuvant materials have been formulated to enhance penetration into the target organisms. Thirdly, the area involving only insecticides is that of making the spray material more attractive to insect pests. The use of flavors, taste enhancers, and pheromones are but a few of the products that have been utilized for this purpose.
3. **To comply with legal requirements.** Many pesticides registered by the Environmental Protection Agency have recommendations for adjuvant use. Depending on the language of the recommendation, the use could be required or suggested. Additionally, there are some geographic or state statutes requiring the use of certain adjuvants with certain pesticides. These usually involve cotton defoliants, hormone herbicides, and drift-reducing adjuvants.

From a personal, as well as an industrial standpoint, it is felt that the utility of adjuvant materials can significantly contribute to the production of agricultural commodities. Within the context of the previously mentioned requirements of minimizing losses and maximizing performance, adjuvant products certainly have a place.

## Chapter 47

**CONCERNS WITHIN THE PESTICIDE INDUSTRY RELATING  
TO SPRAY ADJUVANTS**

Allen K. Underwood

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## I. OVERVIEW OF PESTICIDE AND SPRAY ADJUVANT MARKETS

The information on spray adjuvants presented in this chapter relates to all fields where pesticides are used. Although this information is applicable for use with agricultural pesticides, it is equally applicable for use with pesticides in the aquatic, forestry, golf course, municipality, nursery, ornamental, rights-of-way, turf, utility, and other fields. The concerns are the same in all fields. The world pesticide market in 1989 was estimated to be \$20 billion. The U.S. represents the single largest market, making up 25% (\$5 billion) of the world's total. Pesticide use in the U.S. closely resembles the use of pesticides worldwide. Herbicides dominate the use (44% of total), followed by insecticides (31%), fungicides (19%), and others (6%). In the U.S., registration and regulation of pesticides is carried out under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of the Environmental Protection Agency (EPA) and the Federal Food, Drug and Cosmetic Act.

Sales of emulsifiers and spray adjuvants in the U.S. in 1989 were estimated to be \$300 million. This represents a total of 6% of the U.S. pesticide market. Emulsifiers comprise an estimated \$150-million market. Emulsifiers, for the most part, are the realm of basic raw material supplier companies (e.g., DeSoto, Inc.; Henkle Corp.; ICI Americas, Inc.; Stepan Co.; Witco Corp.) or basic manufacturers of pesticides (e.g., E. I. du Pont de Nemours & Co., [Du Pont]; ICI Americas, Inc.; Rohm and Haas Co.). The formulator or distributor segment of the marketing organization does not have an influential role in this area.

Spray tank adjuvants also comprise an estimated \$150-million market. These products are primarily the realm of the formulator/distributor (e.g., Helena Chemical Co.; Loveland Industries, Inc.; Riverside/Terra Corp.; Wilbur-Ellis Co.). However, some basic manufacturers of pesticides also market spray adjuvant products. These include BASF Corp.; Dow Elanco and Co.; Rohm and Haas Co.; and Valent U.S.A. Corp.

The spray adjuvant market can be divided into two distinct markets: (1) the competitive displacement-market and, (2) the non-use market. The non-use market is potentially much larger than the spray adjuvant market that exists today. In general, formulators and distributors manufacture and market a complete line of spray adjuvant products, while basic manufacturers of pesticides market only one or two specific types. It has been suggested that one reason there are more formulator/distributor products in the market than basic manufacturer's products is the lack of proprietary chemistry and therefore the lack of patentability of the products by the basic manufacturers.

The use of spray adjuvants parallels the use of pesticides. Where there is heavy use of pesticides, there is heavy use of spray adjuvants. Therefore, the major areas of adjuvant usage are in the coastal perimeter states, the southwest, mid-south, northeast, and midwest states. Common links between pesticide usage and spray adjuvant usage are that all fields use pesticides (and therefore spray adjuvants) and water is the primary carrier.

Pesticide labels are the most readily available source of spray adjuvant recommendations. Pesticide labels recommend spray adjuvants for one of two reasons, or both: (1) to increase pesticide efficacy and (2) to reduce, minimize, or eliminate spray application problems. The anticipated result of using spray adjuvants is to reduce the risk of pesticide nonperformance and reduce the risk of crop injury.

## II. TRENDS

As pesticide formulations change and environmental concerns become more of an issue, the need for different types of adjuvants is increased. Pesticide formulations have changed from dusts to emulsifiable concentrates, to flowables, to water-dispersible granules, to



soluble powders. These changes have dictated changes in the amounts and types of emulsifier systems contained within the formulation, plus changes in the use of tank mix spray adjuvants.

Where earlier formulations of pesticides were used at application rates of pounds per acre, many of today's pesticides are used at application rates of grams per acre. Use of pesticides at these small rates necessitates the use of spray adjuvants to provide thorough, uniform coverage of plant parts, to reduce the amount of pesticide active ingredient (a.i.) lost by evaporation and drift, to ensure pesticide effectiveness by preventing alkaline hydrolysis caused by the breakdown of pesticide a.i. in alkaline spray solutions, and to provide other functions needed for maximum pesticide impact. In addition, the new types of pesticides introduced into the market (e.g., synthetic pyrethroids, sterol-inhibiting fungicides, sulfonylureas, etc.) require different types and amounts of spray adjuvants.

The use of spray adjuvants with fungicides, insecticides, biostimulants, and biologicals will increase the total use now dominated by spray adjuvants with herbicides. The same benefits adjuvants provide to herbicides are being realized with the other types of pesticides.

Another trend is for states to begin regulating the use of adjuvants. This is happening in lieu of the EPA requiring the registration and regulation of spray adjuvant products. It is this regulation (or lack of it) that occasioned the development of this chapter. As spray adjuvant use increases, there is legitimate concern that the products should be registered and regulated as are the pesticides with which they are used. If the spray adjuvant industry does not address these concerns and use self-policing action to ensure the effective and safe use of them, then surely it will be done for them.

The balance of this presentation will address specific concerns of the industry. Although these concerns are driven by the marketing end of the business, science and education will determine how successfully these concerns are addressed.

### III. CONCERNS

#### A. NEEDS

One of the major concerns within the industry is determining the need for spray adjuvants. Presently, the single best source for determining this need is the EPA-registered pesticide label.

Other sources include basic manufacturers' technical literature, state extension service recommendations, promotional literature, and research data. Any promotional material authorized by the basic manufacturer can be interpreted as an extension of the pesticide label. Therefore, advertising and promotional literature can be considered a source of information. Adjuvant information contained in an EPA-registered pesticide's label is the preferred source, but that, too, has its concerns. All EPA-registered pesticides contain the following statement: "It is a violation of Federal Law to use this product in any manner inconsistent with its labeling". Although the adjuvant itself is not regulated by the EPA, its use as the result of recommendations on an EPA-registered pesticide label is. Spray adjuvant use in conflict with those specific directions can constitute such a violation. Although federal inspectors are not actively seeking such misuse, legal people do get involved whenever there is pesticide adjuvant nonperformance or crop injury from pesticide or adjuvant tank mixes. Therefore, careful interpretation of adjuvant recommendations on EPA pesticide labels is important. EPA pesticide labels can be classified according to the adjuvant information contained on them. This information includes the following:

**Very specific recommendations** — These recommendations are noted by the use of such terms as "always add a . . .", "must be used with . . .", "add a . . .", etc.

**Suggested recommendations** — These recommendations are noted by the use of such terms as "should be used . . .", "may be added . . .", "can be . . .", etc.



TABLE 1  
Nonionic Surfactants: A Sampling of EPA-Registered Pesticide Labels  
Containing Recommendations and Suggestions

Trade name	Common name	Registered trademark of
Ambush®	Permethrin	ICI Americas, Inc.
Asana®	Esfenvalerate	E. I. du Pont de Nemours & Co., Inc.
Benlate®	Benomyl	E. I. du Pont de Nemours & Co., Inc.
Classic®	Chlorimuron ethyl	E. I. du Pont de Nemours & Co., Inc.
Diquat®	Diquat	Chevron Chemical Co.
Dithane®	Dithiocarbamate	Rohm and Haas Co.
Dropp®	Thidiazuron	Nor-Am Chemical Co.
Goal®	Oxyfluorfen	Rohm and Haas Co.
Fusilade® 2000	Fluazifop-P-butyl	ICI Americas, Inc.
Gramoxone Super®	Paraquat	ICI Americas, Inc.
Pursuit®	Imazethapyr	American Cyanamid Co.
Roundup®	Glyphosate isopropylamine salt	Monsanto Agricultural Co.

**Labels void of adjuvant recommendations or suggestions** — These labels contain no specific or inferred reference to the use of adjuvants. Likewise, they contain no specific prohibitions.

**Labels with specific prohibitions** — These labels are noted by terms such as “do not add any additional . . .”, “do not use with . . .”, “do not tank mix with . . .”, etc.

**Tank-mix recommendations and suggestions** — These labels, when the product is used alone, can make specific recommendations or suggestions for adjuvant use, or can even be void of such recommendations. However, when the product is used as one component of a tank mix with other pesticides, nutrients, or fertilizers, the adjuvant recommendations change dramatically. When two or more products are used in a tank mix, the product label containing the most restrictive recommendation takes precedence.

**Combination of all recommendations** — Some pesticide labels contain instructions that utilize each type of information noted previously.

A review of hundreds of EPA pesticide labels has revealed that the labels of over 200 commonly used pesticides have very specific recommendations or suggestions for the use of one, and sometimes as many as six spray adjuvants. Many of these same labels also contain various combinations of the information detailed above.

From the adjuvant information compiled as a result of these label reviews, adjuvant abstracts were made for each pesticide, which included the exact recommendations and suggestions contained on the label. The abstracts were then used to identify, by brand name or adjuvant type, the various adjuvant products that were suitable for use.

From these abstracts, an adjuvant-pesticide cross-reference chart was formed. This chart allows a pesticide user to quickly determine what adjuvants, if any, are recommended for use with specific pesticides. If several were recommended, he could then cross-reference the adjuvant abstract for more complete, specific information, or consult the pesticide label for information on his specific crop, equipment, tank mix, etc.

After the cross-reference chart had been completed, it was easy to make lists of pesticides that required specific types of spray adjuvants. Tables 1 through 4 list several major pesticides whose labels recommend very specific uses of the adjuvant types noted. The label of each product must be reviewed to determine the exact use instructions.

Several trends can be determined from these tables. Nonionic surfactants and crop oil concentrates are generally recommended with herbicides, while “spreader-stickers” are generally recommended with insecticides and fungicides. Also, some herbicide labels rec-

**TABLE 2**  
**Crop Oil Concentrates (Oil Concentrates): A Sampling of EPA-Registered Pesticide Labels Containing Recommendations and Suggestions**

Trade name	Common name	Registered trademark of
Aatrex®	Atrazine	Ciba-Geigy Corp.
Basagran®	Bentazon	BASF Corp.
Blazer®	Acifluorfen	BASF Corp.
Classic®	Chlorimuron ethyl	E. I. du Pont de Nemours & Co., Inc.
Dropp®	Thidiazuron	Nor-Am Chemical Co.
Evik®	Ametryn	Ciba-Geigy Corp.
Fusilade® 2000	Fluazifop-P-butyl	ICI Americas, Inc.
Gemini®	Linuron + chlorimuron	E. I. du Pont de Nemours & Co., Inc.
Pix®	Mepiquat-chloride	BASF Corp.
Poast®	Sethoxydim	BASF Corp.
Scepter®	Imazaquin	American Cyanamid Co.
Whip®	Fenoxaprop-ethyl	Hoechst-Roussel Agri-Vet Co.

**TABLE 3**  
**Spreader-Stickers: A Sampling of EPA-Registered Pesticide Labels Containing Recommendations and Suggestions**

Trade name	Common name	Registered trademark of
Benlate®	Benomyl	E. I. du Pont de Nemours & Co., Inc.
Ambush®	Permethrin	ICI Americas, Inc.
Asana®	Esfenvalerate	E. I. du Pont de Nemours & Co., Inc.
Bravo®	Chlorothalonil	Fermenta ASC Corp.
Dipel®	<i>Bacillus thuringiensis</i> var. <i>Kurstaki</i>	Abbott Laboratories
Dithane®	Dithiocarbamate	Rohm and Haas Co.
Karate®	Shaughnessy 128867(a)*	ICI Americas, Inc.
Larvin®	Thiodiacarb	Rhone-Poulenc
Manzate®	Dithiocarbamate	E. I. du Pont de Nemours & Co., Inc.
Orthene®	Acephate	Chevron Chemical Co.
Ridomil®	Metaxyl	Ciba-Geigy Corp.
Vendex®	Fenbutatin oxide	E. I. du Pont de Nemours & Co., Inc.

\* Code number.

**TABLE 4**  
**Compatibility Agents: A Sampling of EPA-Registered Pesticide Labels Containing Recommendations and Suggestions**

Trade name	Common name	Registered trademark of
Ambush®	Permethrin	ICI Americas, Inc.
Asana®	Esfenvalerate	E. I. du Pont de Nemours & Co., Inc.
Aatrex®	Atrazine	Ciba-Geigy Corp.
Balan®	Benefin	Dow Elanco and Co.
Benlate®	Benomyl	E. I. du Pont de Nemours & Co., Inc.
Bicep®	Atrazine + metolachlor	Ciba-Geigy Corp.
Dual®	Metolachlor	Ciba-Geigy Corp.
Lasso®	Alachlor	Monsanto Agricultural Co.
Lorsban®	Chlorpyrifos	Dow Elanco and Co.
Princep®	Simazine	Ciba-Geigy Corp.
Scepter®	Imazaquin	American Cyanamid Co.
Treflan®	Trifluralin	Dow Elanco and Co.

commend either nonionic surfactants or crop oil concentrates, while other herbicides are very specific in their recommendation of only one of the two types. Nonionic surfactants are recommended with almost every type of pesticide, e.g., herbicides, fungicides, insecticides, plant growth regulators, etc. Nonionic surfactants as a type dominate all spray adjuvant recommendations, followed at a distance by oil concentrates or crop oil concentrates. Similar tables can be made for the other types of spray adjuvants.

From the information presented above, it is clear that spray adjuvants are recognized by the basic manufacturers as an important component in the final spray mixture of many widely used pesticides. However, many concerns are expressed by basic manufacturers, extension service representatives, distributor representatives, and pesticide users as to the validity of these recommendations. This is largely due to the spray adjuvant products themselves not being regulated by the EPA (or any other agency), as are the pesticides with which they are used. The regulation of pesticides, inert ingredients contained within pesticide formulations, and pesticide solvent-emulsifier systems have been discussed in detail at the two international symposia on adjuvants for agrichemicals. Little information has been presented on how to effectively address the concerns of the spray adjuvant industry in validating the proper position and need of spray adjuvants within the pesticide industry.

#### **B. REGULATION**

Regulation, or more specifically the lack of regulation, is another concern of the industry. As noted previously, the use of spray adjuvants is not regulated by the EPA, as are the pesticides with which they are used. The only regulation of spray adjuvants is that the components of the spray adjuvant itself must be exempt under EPA CFR 40, 180:1001(c). That, plus the statement, "It is a violation of Federal Law to use this product in a manner inconsistent with its labeling", which appears on all EPA registered products, is the reason for the concerns presented by this author. Are adjuvant recommendations on pesticide labels to be considered as EPA-labeled tank-mix recommendations and regulated accordingly? Is it a "violation of Federal Law" if the pesticide is used properly, but the spray adjuvant used with the pesticide is different from the pesticide's label recommendation? Does a pesticide label's suggested use of a spray adjuvant carry the same weight as a specific spray adjuvant recommendation?

Some states (e.g., California, Mississippi, and Arkansas) have spray adjuvant regulations that exceed the EPA regulations. This adds to the concern that if the EPA or our own industry does not provide suitable regulation, then each state, basic manufacturer, or distributor may have its own set of regulations. Based on previous experience with this "scattered" method of regulation of pesticides, fertilizers, nutrients, soil admendments, and others, this is not in the best interest of the pesticide user or spray adjuvant industry.

#### **C. TERMINOLOGY**

Terminology is always a challenge to clear communication; for example, there are at least six different published definitions for the term "spray adjuvant". It is even more confusing to properly define the different types of spray adjuvants, the chemical and physical differences of spray adjuvants, and the benefits of spray adjuvants. The terms "surfactant" and "adjuvant" are often used interchangeably, and it is difficult to determine if authors are talking about "oils", "crop oils", or "crop oil concentrates" since they are not clearly defined in the presentations and are often used interchangeably themselves. One can readily define "wetting" and "buffering", but no good definitions apply to "penetration" and "sticking". A thorough review and subsequent standardization of adjuvant terminology is needed.

#### D. TESTING

Since adjuvant products are not seriously regulated, adjuvant suppliers constantly add new products into an already confused marketplace. Many of these products do not have adequate, if any, testing to determine their influence on the activity of the pesticide or the crop to which it is applied. A review of data and the testing of a series of adjuvant types and several products within each type has led to the following conclusions:

- Spray adjuvants are pesticide specific.
- Spray adjuvants are a.i. specific.
- Spray adjuvants are crop specific in terms of crop injury.
- Spray adjuvants are phytotoxic to specific crops at certain stages of development, but nonphytotoxic to the same crop at other stages of development.
- Spray adjuvants are weed species, insect species, and pest species specific.
- Spray adjuvants are type specific.
- Spray adjuvants are rate specific.
- Spray adjuvants are pesticide tank-mix specific.
- Spray adjuvants are carrier-volume specific.
- Spray adjuvant activity can be partially determined by its order of addition into the spray tank.

Only scientific testing will determine a pesticide or crop reaction to a spray adjuvant. Due to the tremendous number of types, and differences between products within types, such testing will not be done by the basic manufacturers or distributors unless proprietary chemistry is developed or the industry stiffens certain regulations.

Although researchers have generated an abundance of adjuvant data, it is difficult to create a database from it because the researchers used:

- The wrong type of adjuvant, i.e., crop oil rather than crop oil concentrate
- The wrong rate of spray adjuvant
- An adjuvant whose formulation changes substantially from batch to batch, region to region, and year to year
- An adjuvant that is not commercially available
- A commercially available adjuvant product in testing, but generic terminology in reporting the results
- A spray adjuvant that was not specific for situations as detailed above

These are some of the concerns that need to be addressed in testing adjuvant products.

#### E. COMMUNICATION

Communication of adjuvant information is important to the industry. Who is going to do it, and is it going to be done properly? As a general rule, the EPA does not provide much information about products/programs they do not regulate. Basic manufacturers, extension service representatives, and consultants are more concerned with communicating information relating to the pesticide's a.i. Pesticide distributors heavily promote their adjuvant products, but many lack appropriate data and use terminology that is wrong or confusing.

For the many pesticides that require the use of a spray adjuvant, "error of omission" is as much a problem as the poor job of communicating the positive information. Volumes of documents and hours of discussion are available on these pesticides, but their mandatory use with a specific type and rate of spray adjuvant is seldom noted. This creates confusion



TABLE 5  
Crop Oil Concentrates:  
Variation in % Active Among  
Products Within Type

Product	% Active
A	98.3
B	92.4
C	49.4
D	99.2
E	98.3

in the pesticide user's mind when confronted with a recommendation to use a specific spray adjuvant with a specific pesticide.

It is a concern of the spray adjuvant industry that the most readily available adjuvant information is obtained by reading vague or confusing adjuvant recommendations on EPA-registered pesticide labels or by attending international symposia on spray adjuvants for agrichemicals.

#### F. EVALUATION

Another concern of the adjuvant industry is evaluation, in terms of efficacy, as well as physical and chemical characteristics. Evaluation methods are available for most needs, but the industry as a whole does not use them, and will not until there is more regulation. Efficacy evaluation has already been discussed in Section III.D. Physical and chemical characteristics and the methods for evaluating them have been covered in detail in other chapters. Concerns other than evaluation methods will be discussed here.

Some pesticide labels make very specific recommendations for the use of a crop oil concentrate (COC)-type spray adjuvant. The use of a given pesticide, even with a COC, can result in nonperformance and crop injury due to the wide range of activity among products of the same type. Table 5 illustrates this point.

It was claimed that the five products listed in Table 5 were COC-type products or could be used to replace a COC product. A simple evaluation utilizing an American Society of Test Materials (ASTM) evaluation method shows the variability among the products. If all five products were evaluated with pesticides that specifically recommended COC-type products, one would expect to obtain variable efficacy results. A common definition of a COC requires it to contain 80 to 85% petroleum or vegetable oil and 15 to 20% emulsifier. At a minimum, a COC would contain a total of 95% a.i. Utilization of the ASTM test for volatility shows that three products meet the recommendation, while one is close to the minimum level and another is drastically off the mark.

Further evaluation of these five products showed that products A, D, and E formed stable emulsions, while product B formed a weak emulsion and product C caused a precipitation of the pesticide a.i. This precipitation of pesticide a.i. can result in unacceptable degrees of crop injury, and the weak emulsion characteristics can result in nonperformance. These emulsions were tested for stability at 3, 5, 7, and 15 min after mixing.

Evaluation of products claimed to be nonionic surfactants utilizing the same ASTM test resulted in the following information (Table 6). Wide variability in "% active" was again found, and upon further evaluation, product E was found to be ionic, not nonionic. If these six products were tested for efficacy with pesticides whose labels specifically recommended the use of nonionic surfactants, one could expect highly variable results. Many EPA-registered pesticide labels make very specific recommendations as to the amount or percent of "surface active agent" or "active ingredient" a spray adjuvant must contain. One group



**TABLE 6**  
**Nonionic Surfactants:**  
**Variation in % Active Among**  
**Products Within Type**

Product	% Active
A	81.4
B	40.4
C	80.2
D	49.4
E	46.3
F	74.4

of pesticides requires a minimum of 80% a.i. while another group recommends 75% a.i. Very few pesticides recommend the use of 50% (or less) a.i. but at higher rates. From this evaluation, only products A and C meet the 75 to 80% a.i. recommendation, while product F is borderline and products B, D, and E could not be used.

Additional evaluations of these nonionic surfactants showed great variability in the ability of the products to wet, spread, adhere, and penetrate. This range of activity within the adjuvant type can lead to pesticide nonperformance, crop injury, and liability situations. Such variability among products within the same type of spray adjuvant is a major concern.

#### **G. VARIABILITY**

Variability of spray adjuvant products is a concern; whereas the pesticide industry has a check and balance system for product quality, the spray adjuvant industry does not. This is evident in the variability of the formulation and composition of commercially available products. Reasons for this variability can be traced to the way adjuvants are made. Different adjuvants are formed by chemical modifications to the hydrocarbon chain, the water-soluble head, or both. In addition to these modifications, nonsurfactant components can be added. Such modifications and additions can result in tremendous changes in spray adjuvant activity. Although they carry identical labels, some products change in almost all measurable physical and chemical characteristics. This includes products that:

- Have varying and wide-ranging percentages of a.i.
- Have varying ratios of oil and emulsifier components
- Have different inerts
- Change from one batch code number to another
- Change from one formulation to another on a regional basis
- Change from one formulation to another on a yearly basis

One report from the Arkansas State Plant Board's inspection program found eight samples of identically labeled spray adjuvant products that ranged from 5 to 60% a.i. The products were labeled as 80% active. This variability in spray adjuvant composition can have a tremendous effect on pesticide performance and crop safety. Until regulation minimizes this variability, it will continue to be a major concern within our industry.

#### **H. LIABILITY**

The liability associated with the use and non-use of spray adjuvants is another concern within the industry. As it is understood by this author, if an EPA-registered pesticide label does not make a specific recommendation for the use of a specific spray adjuvant, but on the other hand does not make a specific prohibition of a specific adjuvant, then any spray

adjuvant can be used. However, the liability of pesticide nonperformance and crop injury is shifted from the basic manufacturer to the applicator. Given the concerns outlined in this chapter, one can see that the use of spray adjuvants outside of specific EPA label recommendations is risky, for both the formulator and the end user.

Results of spray adjuvant use to increase pesticide efficacy are easier to monitor than results of spray adjuvant use to affect the numerous spray application problems. Until the liability situations of spray adjuvant use are more clearly defined, it will remain a major concern within our industry.

### I. SPRAY ADJUVANT LABELING

Spray adjuvant labeling is a major concern within our industry. Because of the lack of regulations discussed previously, commercially available spray adjuvants are found where:

- The percent a.i. in the formulation is quite different from that guaranteed on the label
- All active ingredients within the formulation are not identified
- The ionic classification is not noted, or the product claims to be one ionic class when it actually is another
- The spray adjuvant is noted as a specific type when in actuality it is a different type
- The product is not noted as being exempt under the EPA's CFR 40, 180.1001(c)
- The product label carries aquatic recommendations even though aquatic toxicology studies have not been performed
- The label makes vague recommendations
- The label makes nonverifiable claims

Adjuvant labels are written, for the most part, by formulators and distributors, not by basic manufacturers. The difference in structure and content between EPA-registered labels and spray adjuvant labels is readily evident. Until spray adjuvant labeling advances at least to the form and content of pesticide labels, it will remain a major concern within our industry.

### J. PESTICIDE LABEL RECOMMENDATIONS

It is evident from a review on EPA-registered pesticide labels that the labels are confusing. It is suggested that if pesticide labels were more consistent and specific in their recommendations, suggestions, and prohibitions, the formulators and distributors would do a better job of writing their own labels. Some basic manufacturers have recognized the problem and have attempted to deal with it. Others have not yet recognized the problem, and their labels reflect that! A few examples will illustrate this point. Information contained in small print is directly from the EPA-registered pesticide label.

#### Example A

Trade name	Assure®
Common name	quizalofop-ethyl
Registered trademark	E. I. du Pont de Nemours & Co., Inc.

Always include a spray adjuvant with postemergent applications. Petroleum Oil Concentrates should be of good quality and contain a minimum of 15% emulsifier or surfactant. Nonionic surfactants should contain at least 80% active ingredient. USE ONLY EPA APPROVED OIL CONCENTRATES AND SURFACTANTS.

This is an example of very specific recommendations for use, types, and, to a certain extent, quality. The amount of a.i. is noted for both the nonionic surfactant and the COC. However, confusion is created when the label recommends, "Use only EPA approved . . .".

Since adjuvants are not regulated or "approved" by the EPA, would the use of any adjuvant with this product be in violation of the label?

### Example B

Trade Name	Basagran®
Common name	bentazon
Registered trademark	BASF Corp.

The oil concentrate must contain either a petroleum or vegetable oil base and must meet the following criteria:

1. Be non-phytotoxic
2. Contain only EPA exempt ingredients
3. Provide good mixing quality in jar test
4. Be successful in local experience

This label excerpt is very specific for the type recommended and the parameters needed of the products within the type. Additional label information is provided to help the user make a decision on the best product within the type.

The label further states:

An ideal tank mix combination will be uniform; thus, the suitability of the oil concentrate is questionable if any of the following are observed:

- Free oil at the surface — film or globules
- Flocculation — fine particles suspended in liquid or found as precipitated layer at bottom of jar
- Clabbering — thickening texture (coagulated) resembling yogurt or cottage cheese

Furthermore, the label points out that there are differences between products within the type and warns the user as to what will happen if he chooses the wrong one: "The exact composition of suitable products will vary; a few oil concentrates have exhibited excessive leaf burn". This information indicates that the basic manufacturer realizes that there is variation in the composition of products within the type, and even though the customer chooses the correct type, crop injury could still result.

### Example C

Trade name	Roundup®
Common name	glyphosate isopropylamine salt
Registered trademark	Monsanto Agricultural Co.

Nonionic surfactants which are labeled for use with herbicides may be used. When label instructions require the use of surfactant, use 0.5 percent concentration when using surfactants which contain at least 50 percent active ingredient, or 1 percent concentration for those containing less than 50 percent active ingredient.

This label allows for the use of different-quality surfactants, but at very different rates. In addition, it depends upon a formulator's surfactant label recommending use with herbicides rather than one cleared for use on growing crops under 40 CFR 180.1001(c). Also, this label information indicates that the basic manufacturer recognizes a tremendous range in the percent of a.i. within the surfactant group.

**Example D**

Trade name	Gramoxone Super®
Common name	paraquat
Registered trademark	ICI Americas, Inc.

Always add a nonionic surfactant (approved for use on growing crops) containing at least 50% surface active ingredient. FAILURE TO USE A NONIONIC SURFACTANT AT RECOMMENDED RATES WILL RESULT IN REDUCED PERFORMANCE.

This label is very specific in type and quality, and defines the consequences of misuse. It also points out that some basic manufacturers will lower the requirements of their recommendations to accommodate the use of low-percent active spray adjuvant products.

**Example E**

Trade name	Fusilade® 2000
Common name	fluazifop-P-butyl
Registered trademark	ICI Americas, Inc.

**ALWAYS ADD ONE OF THE FOLLOWING:**

- Crop Oil Concentrate — Add a non-phytotoxic crop oil concentrate or a once-refined vegetable oil concentrate containing 15-20% approved emulsifier . . .
- Nonionic Surfactant — Add a nonionic surfactant containing at least 75% surface active agent . . .
- Spray Additives — Only crop oil concentrates and nonionic surfactants cleared for use on growing crops under 40 CFR 180.1001(c) may be used in spray mixtures.

This label is very specific in type and quality, and further specifies that the product must be cleared for use on growing crops.

**Example F**

Trade name	Asana®
Common name	esfenvalerate
Registered trademark	E. I. du Pont de Nemours & Co., Inc.

Add adjuvant (X-77, Bio-88, Unite, Triton B-1956 or equivalent) to spray tank . . .

The brand names recommended on this label are those of wetters, spreaders, activators, compatibility agents, and stickers. Also, ionic classification is not specified, although both nonionic and anionic products are recommended. This label, by using an assortment of brand names and then stating "or equivalent", allows for the use of almost any additive.

**Example G**

Trade name	Ally®
Common name	metasulfuron-methyl
Registered trademark	E. I. du Pont de Nemours & Co., Inc.

Unless directed otherwise, use a surfactant of at least 80% active ingredient . . . Anti-foaming agents may be needed. DO NOT use liquid fertilizer in addition to or as a substitute for a surfactant.

This label gives very specific instructions, then a suggestion, then a prohibition. This is the type of information an end user needs to make the decisions necessary for maximum results from pesticide sprays. However, by not stating the ionic classification of the surfactant

recommended, nonionic, cationic, anionic and amphoteric surfactants could be used, most assuredly with variable results.

**Example H**

Trade name	Evik®
Common name	ametryn
Registered trademark	Ciba-Geigy Corp.

... add a nonionic surfactant such as DuPont WK, X-77, LOC, X-114 or ACL209 or a crop oil concentrate such as Agri-Dex, Amoco or Unico ...

This label recommends two different types of spray adjuvants, but only three of the eight products listed are commercially available. Confusion can occur when sales representatives try to switch their customers' request for one name or type to another.

These are just a few examples of pesticide label recommendations and suggestions that cause concern within our industry.

#### IV. SUMMARY

As long as all EPA-registered pesticide product labels carry the statement, "It is a violation of Federal Law to use this product in a manner inconsistent with its labeling", and as long as spray adjuvant products are not regulated as are the pesticides with which they are used, these concerns, and others, will be the basis for interaction among academia, researchers, basic manufacturers, extension specialists, consultants, formulators, dealers, salesmen, and consumers that will eventually lead the spray adjuvant industry to such a level that the true benefits of high-quality spray adjuvants are recognized and the maximum impact from the lowest effective labeled pesticide dose can be realized. Significant environmental and economic benefits could result.



## Chapter 48

**A REVIEW OF THE METHODOLOGY EMPLOYED IN THE  
LABORATORY EVALUATION OF SPRAY ADJUVANTS**

Johnnie R. Roberts

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## I. INTRODUCTION

Most of the agrichemicals currently utilized in modern agriculture require some type of spray adjuvant. In the U.S. market alone, over 200 pesticides have label requirements for one or more spray adjuvants.<sup>4</sup> In most cases, adjuvants are used to maximize their efficacy and ease of application. Some agrichemicals, however, can exhibit nonperformance if the specified adjuvant is omitted or an inappropriate one substituted.

In addition to satisfying established label requirements and recommendations, adjuvants are evaluated in various spray applications which have exhibited failures due to one or more "real-world" variables. Examples of such variables include coverage, drift, water quality (pH and ionic content), evaporation, and water washoff of the applied agrichemical. On many occasions, adjuvants are used to mitigate or correct the problems caused by such variables.

The current political and economic climate in which agricultural chemicals are used mandates that future efforts to enhance performance rely on achieving the most efficacious minimum use rates. Obtaining higher levels of efficacy would provide benefits which are both economically and environmentally sound. There is a growing awareness that spray adjuvants have a role in achieving this goal.

The factors above, among others, have resulted in a diverse and confusing array of adjuvant compositions and claims. It is reported that in the U.S. alone, over 300 companies offer 4000 adjuvants.<sup>2</sup> This is compounded by the fact that regulatory guidelines regarding adjuvant claims and definitions are usually absent or insufficient.

As a consequence, actual field trials are the only means available to both verify and evaluate adjuvant label claims. The high costs and time considerations associated with such field trials, however, make laboratory evaluations an important screening procedure for these products.

In addition, these procedures are useful in verifying that adjuvant compositions meet the specifications established by the pesticide labels requiring them. It is reasonable to assume that the adjuvant specifications established by these product labels were made after field trials or past experience. Following these guidelines should prevent or alleviate problems due to nonperformance, crop injury, spray mix incompatibility, and poor application.

This chapter presents an overview of the methods currently utilized in the laboratory evaluation of spray adjuvants. Applicable standardized and referenced methods will be discussed along with the limitations associated with them. Suggestions are made on how to address these limitations and what modifications, if any, are required in order to utilize them in adjuvant evaluations.

Several adjuvant physical and chemical properties lend themselves to evaluation by standardized laboratory procedures. The use of such standardized procedures is vital in order to ensure that the values obtained are both reproducible and valid. Fortunately, several of these procedures are available from the American Society of Test Methods (ASTM).

Procedures lacking official standardization are also applicable, provided they are both referenced and reproducible. Table 1 lists adjuvant physical and chemical parameters along with methods meeting the guidelines established. A discussion follows regarding the limitations of these procedures and the means of correcting them.

## II. LABORATORY METHODOLOGY

### A. ACTIVE INGREDIENT CONTENT

This parameter is one of the most important with regard to meeting pesticide label adjuvant specifications. Utilizing adjuvant compositions with active ingredient contents lower than those specified increases the chance of nonperformance. The determination of adjuvant

TABLE 1  
Laboratory Procedures Applicable to Spray Adjuvant Evaluation

Parameter	Method	Ref.
Active ingredient	Loss on drying (LOD)	ASTM D176
Water	Karl Fisher titration	Std. method
Alcohols	GLC/FID	AOAC 13th ed., #9.075-9.079
Glycols	GLC/FID	AOAC 13th ed., #35.007
Surface tension reduction	Du Nouy Tensiometer®	Fisher Scientific
Dynamic	Sugden bubble pressure	Sensa-Dyne
Wetting performance (static)	Direct measurement	Adamson, 1976 (1)
Contact angle	Goniometer	McKay, 1985 (8)
Spread diameter	Direct measurement	Schwarz, 1964 (10)
Wetting performance (dynamic)	Draves static wet time	ASTM D2281
Compatibility activity	Pesticide/liquid fertilizer	ASTM STP 943
Emulsion performance	Suspension stability	WHO/SIF/31.R2
Evaporation reduction	Weight loss @ 99°C	ASTM D972
Ionic classification	Qualitative (all)	Berol method 210
Anionic	Quantitative	ASTM D3049
Nonionic	Thiocyanate titration	EST (1977, p. 1167)
Foaming	Ross-Miles	ASTM D1173-53
Defoaming performance	Static	Dow Corning CTM-0003
Defoaming performance	Dynamic	Dow Corning CTM-0700

active ingredient content is complicated, however, due to the complex compositions of adjuvants currently on the market. Unlike pesticides, most of the active ingredients in these formulations do not lend themselves readily to direct analysis. It is much easier, therefore, to determine how much of the product is inactive and assume that the remainder is active ingredient.

The inactive components or diluents commonly encountered in most spray adjuvants are water and C1 to C4 aliphatic alcohols. A simple loss on drying (LOD) procedure such as that described in ASTM method D176, part II, provides a simple and quick indicator for such diluents. This procedure is utilized by several state regulatory agencies and is generally a reliable indicator of adjuvant active ingredient content. This procedure, however, suffers from three significant limitations:

1. In some instances, low boiling surfactants, which are active ingredients, are driven off and their presence is not reflected by the test.
2. High boiling point inerts such as inorganic salts and glycols can sometimes be counted as active ingredients since they remain after drying.
3. Activity functions exhibited by some adjuvants are not related to the solids content.

If a LOD test provides results which are inconsistent with label claims made by the manufacturer, the following steps are recommended in order to address the limitations of these procedures:

- 1A A Karl Fisher water analysis should be obtained in order to determine the water content.
- 1B Direct measurement of alcohol content should be made using a gas-chromatography method (GLC/FID), such as the procedure of the Association of Official Analytical Chemists (AOAC) #9.075-9.079, 13th edition.
- 1C The values obtained for percent water and percent alcohol should be totaled and compared to that obtained by LOD. If the difference between these values is greater than that of the respective methods margins of error, the LOD activity value should be corrected accordingly.

- 2A The current economics regarding glycols make them unlikely candidates for inactive adjuvant diluents. An indication of their presence is a relatively high specific gravity (1.100 gms/cc to 1.150 gms/cc). Verification of their presence and amount can be made by employing AOAC method 35.007, 13th edition.
- 2B Inactive inorganic fillers should be suggested if the spray adjuvant exhibits a high specific gravity (values greater than 1.200 g/cc). Examination of the residue remaining after an LOD measurement is also a good indicator. The appearance of crystalline particulate matter indicates the presence of such diluents. Typical examples of this type of filler include urea, trisodium phosphate (TSP), sodium chloride, and liquid fertilizers. None of these substances exhibit surfactant properties.
- 3A If the activity function of a spray adjuvant is not related to solids content by LOD, verification of the label inert claim should be made. If the level of inerts (water, alcohol, and glycols) exceeds that guaranteed by the label, the level of products described as active ingredient must be proportionally lower.

#### B. SURFACE TENSION REDUCTION (STATIC)

By utilizing a De Nouy tensiometer, the measurement of surface tension reduction provides a precise and readily obtainable measure of comparison between spray adjuvants. It is important, however, that the values obtained be considered in conjunction with those of other parameters such as spreading, wetting, and dynamic surface tension. This is because it is necessary to distinguish between the efficiency of the spray adjuvant's (i.e., the concentration of adjuvant required to reduce surface tension in some significant amount) and its performance capabilities (i.e., the maximum reduction of surface tension possible). These two criteria are not always complementary and may even hinder each other.

ASTM method #D1331-56 provides the guidelines for use of a Du Nouy Tensiometer®. It should also be noted that low static surface tension values are not always indicative of good spray droplet spreading. For this reason, adjuvant performance comparisons based on surface tension reduction potential are incomplete if values for wetting performance are lacking.

#### C. SURFACE TENSION REDUCTION (DYNAMIC)

Dynamic surface tension values reflect the bounce-back or rebounding effect spray droplets encounter when they hit vegetation. The rebounding effect is a function of mass, velocity, and surface tension. Upon impacting vegetation, spray droplets flatten out and surface tension attempts to pull them back into a sphere. This action results in a strong contribution to the rebound effect.

Spray adjuvants producing low dynamic surface tension values in spray mixes reduce droplet rebounding. These values are readily obtained by utilizing the Sugden bubble pressure method for measuring dynamic (kinetic) surface tension.<sup>11</sup> This method provides the basis for the Sensa-Dyne® Model 6000 surface tensiometer which, in conjunction with an IBM PC, provides the display, retrieval, storage, and graphing of data.

#### D. WETTING PERFORMANCE (STATIC)

Wetting action is described in ASTM standardized definition E270, E-7, as "the ability of a liquid to spread out and adhere to solid surfaces". The capability of spray adjuvants to increase this property in water is one of the primary functions of these products. In light of this, wetting performance evaluations provide a key indication of how these products would perform in the field.

Static or "hard-surface" wetting generally requires that the surface to be wetted is nonporous and the surface area relatively small. These conditions are normally encountered with vegetation, but variables such as alternating porosity (stoma variability) and surface

polarity do vary from plant to plant. It is possible, however, to assess static wetting performance between various adjuvant compositions by following the procedures below.

#### E. CONTACT ANGLE

The ability of a liquid to spread over a solid surface can be measured by determining its contact angle with that surface, and calculated using the liquid's surface tension value. These angles are determined by a number of different techniques.<sup>1,8</sup> The angles can be measured directly by use of a goniometer, or indirectly by measuring the height and diameter of the spray droplet, and assuming it is spherical.<sup>3</sup>

If the performance criterion for spray adjuvants is spreading, the lower the contact angle, the greater the coverage.

#### F. SPREAD DIAMETER

This is a simple, reproducible procedure for evaluating spray adjuvant wetting performance.<sup>10</sup> In this method, a known volume of spray adjuvant solution is applied to the surface under question. The diameter of the resulting coverage is measured after a given amount of time, and compared with that obtained by water only or other adjuvant compositions in water. The greater the diameter of droplet coverage, the greater the degree of surface wetting.

The spread diameter procedure allows one to evaluate spray adjuvant performance directly on the surface in question (plant matter). This would permit laboratory evaluations which are crop or pest specific, since actual samples of the substrate in question could be used in the test.

Both the contact angle and spread diameter procedures are subject to complications which may inhibit the reproducibility of their values. These limitations are discussed in great detail in the references listed. They should be considered possible contributors to any problems encountered with data variability.

#### G. WETTING PERFORMANCE (DYNAMIC)

Vegetation presents two distinct types of surface area for wetting:

1. The outer surfaces of vegetation provide somewhat variable surface characteristics. They are subject to 100% wetting, however, when treated with some adjuvant-water combinations. This type of wetting performance is readily evaluated in the laboratory by means of the contact angle and droplet diameter procedures described earlier. Neither procedure, however, duplicates the environment actual spray droplets encounter on plant surfaces.
2. The inner surface of vegetation presents a difficult substrate for wetting by adjuvants due to its variable degrees of water repellency and porosity. As a consequence, measuring the rate at which a spray adjuvant permeates and wets solid surfaces (dynamic wetting) provides a better indicator of this type of wetting performance.

The inner-surface wetting of plant tissues by spray adjuvants is sometimes designated as "penetration". This is not completely accurate, however, since the interactions between adjuvants and plant tissue are not related to wetting activity alone. This makes the concept of penetration less defined and, as a consequence, not readily subject to simple laboratory evaluations of inner-surface wetting, and should be limited to the appraisal of dynamic wetting measurements.

At the present time, only one standardized procedure is available for the assessment of dynamic or kinetic wetting. This procedure is known as the Draves wet time and is described in detail under ASTM method #D2281. In this procedure, a 5-g cotton skein is attached to a 3-g hook and totally immersed in a tall cylinder of the surfactant solution. The solution



displaces air trapped in the skein by its wetting activity, and when it is finally removed, the skein sinks. The time required for this sinking is recorded and used in evaluating wetting agent performance.

Even though this procedure was developed for applications in the textile industry, it is a useful tool in predicting the ability of agricultural spray adjuvants to permeate a solid surface at a given concentration in a certain amount of time.

The physiochemical basis of this test has been investigated.<sup>7</sup> The investigation revealed that wetting time is a linear function of surfactant concentration when it is employed at concentrations below the critical micelle concentration.

Application of this test to the evaluation of agricultural spray adjuvants should follow the guidelines below:

1. Determine wet time values for both high- and low-use rate recommendations.
2. Adjuvant functions based on solvent interactions between the surfaces of vegetation are not evaluated by this test (e.g., penetration of leaf tissue by oils or surfactants).
3. The presence of dissolved inorganic salts such as fertilizers and micronutrients may alter the wet-time values. Spray adjuvants recommended for such applications should be evaluated in the presence of such products.

#### H. COMPATIBILITY PERFORMANCE

Several adjuvant compositions on the market today are recommended for the resolution of spray-mix incompatibilities resulting from the combination of one or more agrichemicals with or without liquid fertilizers. Problems such as suspension fallout, precipitation, viscosity, and "clabber" are quite often correctable by using one of these compositions, which are generally termed "compatibility agents".

Compatibility performance evaluations currently lack standardized methodology. There is, however, a referenced procedure which provides guidance in this area.<sup>5</sup> The procedure involves a simple test using proportionate quantities of the spray mix components. The results obtained provide an indication of whether or not the compatibility agent(s) are capable of resolving or alleviating the spray mix problem.

#### I. EMULSION PERFORMANCE

Emulsion performance is a parameter which is primarily concerned with oil- and solvent-based spray adjuvant compositions such as crop-oil concentrates. When this type of adjuvant is mixed with water, it must be able to make a uniform and stable spray mix with other agrichemicals. In addition, this uniformity must remain for a sufficient period of time in order to prevent spray mix separation before or after it reaches the application target. Please note, however, that emulsion performance alone should not be interpreted as the only indicator of spray mix efficacy.

A measure of spray mix uniformity is provided by determining the emulsion performance of the spray adjuvant in question. In addition, this evaluation must be made with four other variables in mind:

1. Water hardness variations due to divalent cations have a direct effect on emulsion stability.
2. The adjuvant being evaluated must be compatible with the agrichemicals being applied in the spray mix.
3. Water temperature variations can influence emulsion performance.
4. The addition order followed for one or more of the spray mix components can impact the overall uniformity and stability of the mix.

World Health Organization (WHO) procedure SIF/31.R2 provides guidelines for obtaining emulsion performance evaluations. It also provides avenues for appraising the temperature and water variables as well.

It should be noted that WHO procedure SIF/31.R2 contains no provision for evaluating multiple product spray mixes encountered in field applications. This is readily addressed, however, by simply incorporating proportionate amounts of the other spray mix components and following the evaluation guidelines.

#### J. EVAPORATION REDUCTION

The current trend toward reduced spray volumes and uniform active ingredient distributions by utilizing small droplets has increased the likelihood of spray mix evaporation. For ultra-low-volume (ULV) applications where oil is the carrier, evaporation-stable formulations are readily available. This is not the case, however, for spray applications where water is the carrier. For this reason, several adjuvants have been introduced with recommendations for use in evaporation reduction.

Laboratory evaluation of evaporation reduction performance is hampered by the large number of variables encountered in actual field use. Laboratory procedures having applications in this area are available, but limited when applied to water-based spray mixes.<sup>12</sup> ASTM procedure D972 is applicable although the specified 100°C test temperature is too harsh. Utilizing lower test temperatures (45 to 50°C) does provide some indication of evaporation reduction performance. Variables affecting evaporation rates in the field, such as humidity, wind speed, and spray velocity, however, are not addressed by the laboratory procedures.

The deficiencies cited above prevent the substitution of laboratory evaluations for actual field trials of evaporation reduction spray adjuvants. At the present time, they should be considered only as screening procedures in initial product development and/or as a complement to data generated in the field.

#### K. IONIC CLASSIFICATION

The majority of agricultural spray adjuvant recommendations specify that surfactant active ingredients be "charge neutral" or nonionic. This is primarily due to concerns that the "charged" classes of surfactants such as cationics (+), anionics (-), and zwitterionic ( $\pm$ ) are capable of reacting chemically with the active ingredient. Such reactions can result in precipitation of the active ingredient and subsequent nonperformance and application problems. Several procedures based on color changes produced by cobalt thiocyanate-surfactant interactions are available to verify the ionic class of a particular adjuvant surfactant. The Berol Chemicals #210 procedure provides an excellent qualitative tool for determining ionic class. It separates surfactant classes by producing distinct color changes for each respective group due to interactions with cobalt thiocyanate. In addition, this procedure provides a relative indication of a particular surfactant group's concentration, since the intensity of color produced is directly proportional to the concentration.

The ASTM D3049 procedure provides a means of actually quantifying the amount of anionic surfactant present in a spray adjuvant. This procedure is also useful in adjuvant screening to verify what percent of the product is actually nonionic. A product claimed to be "100% nonionic" would show little or no anionic content by this method.

It should be noted that this procedure is subject to interferences. Fortunately, several procedures are provided in the methodology which prevent or alleviate them.

Another procedure based on cobalt thiocyanate-surfactant interactions has been described.<sup>13</sup> This procedure provides both qualitative and quantitative analysis for nonionic surfactant content. As with the ASTM D3049 procedure, this method provides a direct analysis of the surfactant class in question.

Many adjuvant compositions on the market today contain surfactant mixtures from two or more ionic classes. In order to determine which ionic class predominates, Berol method #210 should be utilized for the first "screening" of surfactant components. When the surfactant ionic groupings are established, ASTM method D3049 should be used. Following these guidelines will ensure that the adjuvant being evaluated satisfies the label recommendations for ionic class.

#### L. FOAMING

On many occasions, increased foaming is an unwanted consequence of utilizing adjuvants in agrichemical spray mixes. Besides the nuisance factor associated with foam generation, it can lead to uneven mixes and impact the efficacy of the applied active ingredient(s). In addition, excessive foam presents exposure hazards to mixer/loaders and applicators.

ASTM procedure D1173-53 (Ross-Miles test) provides a means of assessing the foam contribution adjuvants make to spray mixes. It is recommended that this evaluation be formed on the adjuvant alone, since many agrichemical formulations are heavy foamers themselves.

#### M. DEFOAMING PERFORMANCE

Several adjuvant compositions on the market today are recommended as defoaming agents for agricultural spray mixes. In addition, some products are multifunctional, with both defoaming and one or more other adjuvant functions. These products can be readily evaluated by laboratory procedures.

Dow Corning procedure CTM-0003 provides a means of evaluating the static defoaming activity of spray adjuvants before or after the foam is generated. Dow Corning procedure CTM-0700 is a more rigorous evaluation which utilizes a pump to simulate the field conditions which promote foam generation. As with method CTM-0003, this procedure evaluates both foam prevention and foam removal after generation.

### III. ADJUVANT PARAMETERS WITHOUT ESTABLISHED LABORATORY METHODOLOGY

If one reviews the parameters listed in Table 1, it becomes apparent that several spray adjuvant functional claims lack referenced or standardized methodology. Many of these claims are difficult to evaluate in the laboratory. However, much of this difficulty has nothing to do with methodology, but is a consequence of not defining specifically what these functions are. Examples include:

1. Spray mix, sticking, binding, and rainfastness
2. Penetration
3. Activation of spray mix components
4. Herbicide safeners

Adjuvant function 1, however, does lend itself to laboratory evaluation if the activity being appraised is spray mix adherence to a solid surface. It is possible to design laboratory procedures which provide reproducible values useful in prefield evaluations. These techniques are particularly applicable in evaluating the performance of those products which prevent washoff by means of film formation.

Laboratory evaluations of film forming "spreader-sticker" spray adjuvants follow the guidelines below:

1. The spray mix is prepared with products in amounts proportionate to the label recommendations.

2. A known volume of the spray mix is applied to glass plates or shallow dishes.
3. The spray mix residue is then dried by a sun lamp for a set period of time. (This factor should be considered, since some products require activity by UV light in order to form a film.)
4. The dried residues are then exposed to water spray of controlled pressure and a fixed period of time.
5. The spray mix residue remaining is extracted from the plates and analyzed by procedures applicable to the active ingredient of the spray mix.

The resulting values provide insight into the **relative** ability of the adjuvant in question to inhibit washoff of active ingredient residues. They do take into account the variations spray droplets are exposed to when applied to plant surfaces.

This procedure is also useful in assessing the extent, if any, to which spray adjuvants contribute to **increased** washoff and rewetting of applied pesticide residues. This unintended consequence of using nonionic wetting agents is quite common and should be considered in the overall evaluation of adjuvant performance.

The remaining spray adjuvant functions — penetration, activation, and herbicide safening — do not lend themselves to simple laboratory evaluations due to a lack of functional definitions. Verification of these activities requires actual field evaluations, residue studies, bioassays, and investigations with radiolabeled compounds.

In conclusion, laboratory evaluations provide an important tool in the assessment of agricultural spray adjuvant performance. Even though the limitations associated with them prevent their substitution for actual field trials, they do provide a means of screening the hundreds of products on the market today. They are also vital in assuring that adjuvant compositions meet the specifications established by agrichemical producers and researchers.

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## ORGANIZATIONS

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Association of Official Analytical Chemists (AOAC)  
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## Chapter 49

**THE INFLUENCE OF ADJUVANTS ON HERBICIDAL ACTIVITY  
OF ALLOXYDIM-SODIUM, FLUAZIFOP-BUTYL, AND  
TRIBENURON**

Jens C. Streibig and Per Kudsk

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## ABSTRACT

The phytotoxicity of alloxym-sodium [2-[1-(*N*-allyloxyamino)butylidene]-4-methoxycarbonyl-5,5-dimethylcyclohexane-1,3-dione] and fluazifop-butyl [(±)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid] in barley (*Hordeum vulgare* L.) and [methyl-2-[[[*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-methylamino]carbonyl]amine]sulfonyl]benzoate] in white mustard (*Sinapis alba* L.) was assessed when adding increasing amounts of various surfactants or mineral oils to the spray solution.

In all experiments, the adjuvants promoted the herbicide phytotoxicity increasingly with increasing amounts of surfactants or mineral oils added to the spray solution. A large concentration of a weakly cationic fatty amine ethoxylate resulted in a decrease in fluazifop-butyl activity; the optimum adjuvant concentration in the spray solution was about 1%.

The relationship between the enhanced herbicide potency and the amount of adjuvant added to the spray solution could generally be described by a linear relationship on either the original scale, a semilogarithmic scale, or a double logarithmic scale. These relationships are discussed in order to evaluate a general system for assessing the effect of adjuvants on herbicidal action.

## I. INTRODUCTION

Adjuvants enhance the level of weed control obtained by herbicides and are often used with foliar-applied herbicides.<sup>17</sup> They also synergize herbicides, thereby decreasing usage and perhaps delaying the development of resistant weed biotypes.<sup>5</sup>

In principle, the assessment of the effects of adjuvants on the efficacy of herbicides is based at least on a three-dimensional space, as the biological response is very much dependent upon the dose of the herbicide as well as the concentration of the adjuvant in the spray solution.<sup>14,15</sup> The fitting of a polynomial, however, may be quite difficult,<sup>3</sup> and the parameters are difficult to interpret properly. To overcome these problems, we could apply the parallel-line assay approach.<sup>8,12,16</sup> Briefly, the parallel-line technique implicitly assumes that an array of response curves is identical in all parameters except those determining the horizontal locations of the curves along the dose axis. As pointed out elsewhere,<sup>13,15</sup> this forms a reasonable basis for the assessment of the subtle effects of adjuvants.

Alloxym-sodium and fluazifop-butyl are selective herbicides against grass weeds. Their water solubilities differ: alloxym-sodium has a solubility of 200 g l<sup>-1</sup>, where that of fluazifop-butyl is only 0.0002 g l<sup>-1</sup>, as reported to Duke and Kenyon.<sup>4</sup> These contrasting water solubilities affect the way the herbicides are commercially formulated, and hence their biological activity in response to adjuvants. Tribenuron is a newly developed sulfonylurea herbicide for use in cereals and has a pH-dependent water solubility. It is rapidly degraded in the soil, and therefore phytotoxicity is very much dependent on foliar activity. A recent study has investigated the use of surfactant to improve the rainfastness of tribenuron.<sup>7</sup>

The purpose of this study was to investigate the relationship between the efficacy of certain herbicides in response to increasing amounts of adjuvants in the spray solution.

## II. MATERIALS AND METHODS

The experimental layout of all assays was a randomized block design with three blocks.

In the greenhouse assays, 20 winter barley (cv. Igri) plants were grown in 8-liter pots containing a soil-peat mixture. The seedlings were sprayed at their four-leaf stage (HARDI 4110-12 nozzle, 4.0 bar, and 150 l ha<sup>-1</sup>) with five doses of fluazifop-butyl (FUSILADE® 25% w/v a.i.) and alloxym-sodium (FERVIN®, 75% a.i.) alone or with increasing amount

of Frigate® (a weakly cationic fatty amine ethoxylate), Actipron® (a 97% mineral oil with emulsifier) or Lissapol® (a nonionic alkyl-aryl polyoxyethylene). The seedlings were harvested 3 weeks after spraying.

The growth chamber assays were done by growing 25 *S. alba* (cv. Alba) plants in 6-l pots containing a mixture of peat and sand. The photoperiod was 16 h at 17°C with a 1 h transition to and from a night temperature of 10°C. The seedlings, sprayed at various development stages (HARDI 4110-16 nozzle, 4.0 bar, and 260 l ha<sup>-1</sup>), were harvested 14 d after spraying. The dose-response curve for the herbicide tribenuron (EXPRESS®, 75% DF) alone was used as a reference and consisted of six doses, while the dose-response curves for tribenuron plus various amounts of Extravon® or Citowett® (two nonionic alkyl-aryl-polyoxyethylenes) consisted of five or four doses.

A nonlinear regression model of plant fresh weight (FW) per pot ( $U$ ) on the herbicide dose ( $z$ )

$$U_j^i = [(D - C)/(\lambda + \exp(-2(a + b \cdot \log(R_j \cdot z)))) + C] + \gamma + e$$

was fitted simultaneously within an experiment. The symbol  $\gamma$  denotes a block effect and  $e$  is an error term. To stabilize the variance a transformed both-sides technique was used in which  $\lambda$  was found by preliminary analyses of the assays.<sup>10</sup> The fitting of the regression model has been described elsewhere.<sup>11</sup> The parameters defining the upper limit,  $D$ , at zero dose, the lower limit,  $C$ , at large doses, and  $a$  and  $b$  were all assumed to be the same for the response curves in an experiment. The relative potency parameter,  $R_j$ , for the herbicide dose-response curve without adjuvant in the spray solution was fixed at unity, while the relative potency,  $R_j$  ( $j = 1 \dots 5$ ), for a herbicide dose response curve containing adjuvant was included as a regression parameter.

### III. RESULTS AND DISCUSSION

Tables 1 through 3 show summaries of the regressions of the experiments and Figures 1 and 2 illustrate some of the fitted herbicide dose-response curves. As all dose-response curves within an experiment were assumed to be mutually parallel, the relative potencies in Tables 1 through 3 were constant at any one response level considered.  $ED_{50}$  is a measure of the phytotoxicity of the herbicides without adjuvants.

It is evident from Tables 1 and 2 that fluazifop-butyl was about tenfold more efficacious than alloxym-sodium in winter barley.

A plot of the relative potency of alloxym-sodium or fluazifop-butyl and the amount of Actipron in the spray solution in Figure 3 showed that Actipron had a far greater effect on alloxym-sodium than on fluazifop-butyl activity. Of course, this difference in the efficacy of Actipron cannot be separated from the effect of the basic and virtually unknown formulation constituents in the alloxym-sodium and fluazifop-butyl formulations used here. The relative potency of fluazifop-butyl with Frigate even had a maximum between 1.0 and 4.0% in the spray solution (Figure 4). The relationship appeared to be linear at concentrations below 1% Frigate (Figure 4). Lissapol also increased the activity of fluazifop-butyl, but the relationship was only linear when using a semilogarithmic scale (Figure 5).

Not surprisingly, the  $ED_{50}$  for tribenuron sprayed at the cotyledon stage or at the one-true-leaf stage was smaller than the  $ED_{50}$  sprayed at the two-true-leaf stage (Table 3). The relationship between the relative potency of tribenuron and the amount of Extravon in the spray solution clearly showed that promotion of the herbicidal effect of tribenuron by Extravon increased to a far greater extent when sprayed at the two-true-leaf stage than at the cotyledon stage (Figure 6). The small effect of Extravon at the cotyledon stage could be due to the fact that cotyledons do not have a well-developed cuticle characteristic, as do

TABLE 1  
Summary of Simultaneous Fitting of Barley  
Fresh Weight on Doses of Alloxydim-  
Sodium (75% a.i.) with Increasing  
Percentage of Surfactant in Spray Solution

g/pot (FW)		<i>a</i>	<i>b</i>	ED <sub>50</sub> kg ha <sup>-1</sup>
<i>D</i>	<i>C</i>			
254.8 (10.8)	25.07 (1.41)	-1.553 (0.083)	-2.516 (0.172)	0.241 (0.001)
% Actipron		Relative potency		Confidence interval (95%)
0.000		1.000		—
0.008		1.694		1.527-1.860
0.040		1.782		1.649-1.914
0.200		1.628		1.483-1.774
1.000		1.832		1.646-2.018
5.000		3.776		3.395-4.157

Note: The dose response curve for alloxydim-sodium applied alone is used as a reference. Standard deviations in parentheses; *D*, *C*, *a* and *b*, parameter estimates from the nonlinear regression model as are the relative potency estimates; —, no confidence interval.

true leaves.<sup>9</sup> The slope of the curve for the cotyledon stage was barely significant at the 0.05 level. The relationship between the relative potency of tribenuron and Citowett concentration in the spray solution was log-log linear (Figure 7), as also experienced for alloxydim-sodium and sethoxydim in a previous study.<sup>15</sup>

Apart from the high concentration of Frigate, all surfactants and mineral oils promoted the biological activity of the tested herbicides. The promotion of herbicidal activity could be described by a linear relationship on either the original scale, a semilogarithmic scale, or a double logarithmic scale.

As pointed out elsewhere,<sup>2</sup> it can be shown that although there exists a close relationship between, for example, contact angle, surface tension, and spreading coefficient in some systems, there is not necessarily a good correlation between these physical parameters and herbicidal activity. The relationships in Figures 3 through 7 could perhaps be linked with the work of Baker and Hunt,<sup>1</sup> who tried to determine the effect of the solubility and partition coefficient (octanol/water) of some herbicides, with or without surfactant, on uptake. In studies of isolated phenomena in the absorption process, Hamburg and McCall<sup>6</sup> found consistent relationships between the melting points, partition coefficients, and water solubilities of aryloxyphenoxypropionate herbicides and initial uptake. Further understanding of the subtle effects of surfactant on herbicidal activity probably calls for experiments with several herbicides with different physical properties and known formulation constituents.

Although it is difficult to verify, because numerous doses of herbicide and adjuvant are required, we could tentatively entertain the idea that the synergistic effect of most adjuvants can be described by a sigmoid relationship between relative potency and adjuvant concentration, very much similar to that of a dose-response curve for herbicides. If we wish to compare and/or rank adjuvants according to their effects on herbicidal action in a general

TABLE 2  
Summary of Simultaneous Fitting of Barley  
Fresh Weight on Doses of Fluazifop-Butyl  
(25% a.i.) with Increasing Percentage of  
Adjuvants in Spray Solutions

g/pot (FW)		a	b	ED <sub>50</sub> kg ha <sup>-1</sup>
D	C			
498.2 (23.7)	20.44 (1.78)	-2.764 (0.178)	-1.826 (0.147)	0.036 (0.001)
% Frigate		Relative potency		Confidence interval (95%)
0.000		1.000		—
0.008		1.184		0.606-1.761
0.040		1.327		0.656-1.999
0.200		1.909		0.923-2.894
1.000		2.550		1.625-3.475
5.000		2.113		1.103-3.122
453.7 (21.3)	26.07 (2.35)	-2.976 (0.252)	-2.000 (0.210)	0.033 (0.001)
% Lissapol plus		Relative potency		Confidence interval (95%)
0.0000		1.000		—
0.0016		0.718		0.503-0.934
0.0080		1.219		0.701-1.737
0.0400		1.299		0.786-1.811
0.2000		2.063		1.214-2.911
1.0000		2.313		1.515-3.112
282.7 (15.5)	26.75 (1.63)	-4.142 (0.318)	-2.875 (0.260)	0.036 (0.001)
% Actipron		Relative potency		Confidence interval (95%)
0.00		1.000		—
0.15		1.272		1.135-1.409
0.44		1.327		1.164-1.489
1.33		1.216		1.094-1.337
4.00		2.173		1.955-2.391
12.00		2.911		2.624-3.198

Note: The dose response curve for fluazifop-butyl applied alone is used as a reference. Standard deviations in parentheses; —, no confidence interval.

way, we also are compelled to quantify the rate of change of herbicide toxicity as a function of adjuvant concentration in the spray solution.

### ACKNOWLEDGMENTS

We thank ICI Denmark AS, Schering AS, and Nordisk Alkali Biokemi A/S for supplying the agrichemicals used in this study.



TABLE 3  
Summary of Simultaneous Fitting of  
*Sinapis alba* Fresh Weight on Doses of  
Tribenuron (75% a.i.) with Increasing  
Percentage of Surfactants

g/pot (FW)		a	b	ED <sub>50</sub> g ha <sup>-1</sup>
D	C			
130.5 (15.4)	9.47 (6.51)	-1.041 (0.237)	-1.750 (0.431)	0.254 (0.057)
		Confidence level (95%)		
% Extravon <sup>a</sup>		Relative potency		
0.00		1.000		—
0.01		0.856		0.520-1.193
0.10		1.270		0.755-1.786
0.50		1.306		0.848-1.764
1.00		1.889		1.160-2.619
160.0 (12.3)		-0.126 (0.088)	-1.010 (0.156)	0.750 (0.171)
% Extravon <sup>b</sup>				
0.00		1.000		—
0.01		0.615		0.299-0.931
0.10		0.814		0.148-1.480
0.50		2.906		1.686-4.126
1.00		5.202		3.189-7.215
127.5 (11.8)	11.58 (6.33)	-1.000 (0.198)	-1.466 (0.288)	0.208 (0.042)
% Citowett <sup>c</sup>				
0.00		1.000		—
0.01		0.835		0.570-1.099
0.10		1.015		0.631-1.400
0.50		1.631		1.028-2.234
1.00		1.919		1.196-2.642

Note: The dose response curve for tribenuron applied alone is used as a reference. Standard deviation in parenthesis; —, no confidence interval.

<sup>a</sup> Sprayed at cotyledon stage.

<sup>b</sup> Sprayed at two-true-leaf stage.

<sup>c</sup> Sprayed at one-true-leaf stage.

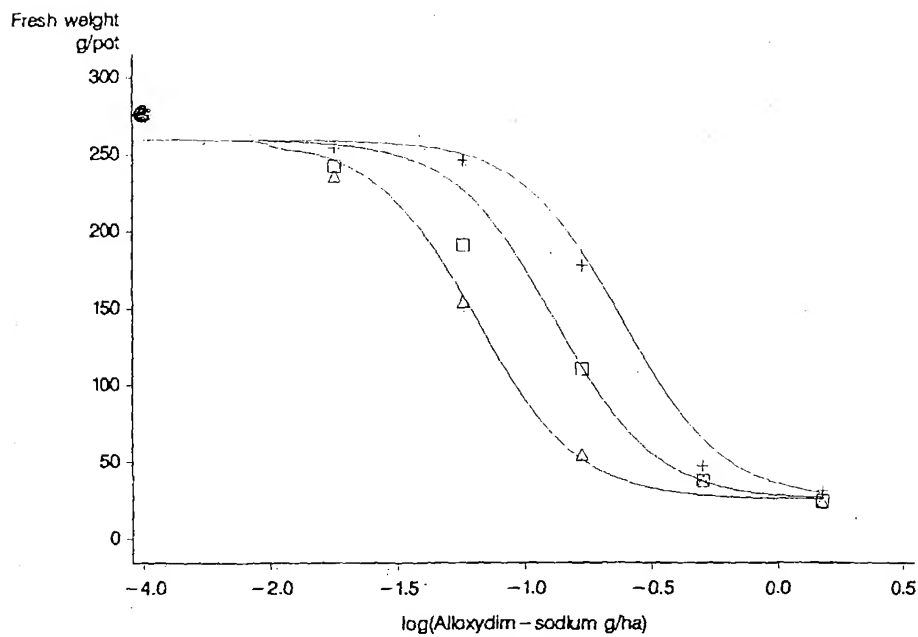


FIGURE 1. Regression of barley fresh weight on alloxym-sodium. (+) Without Actipron; (□) 1% Actipron; (Δ) 5% Actipron.

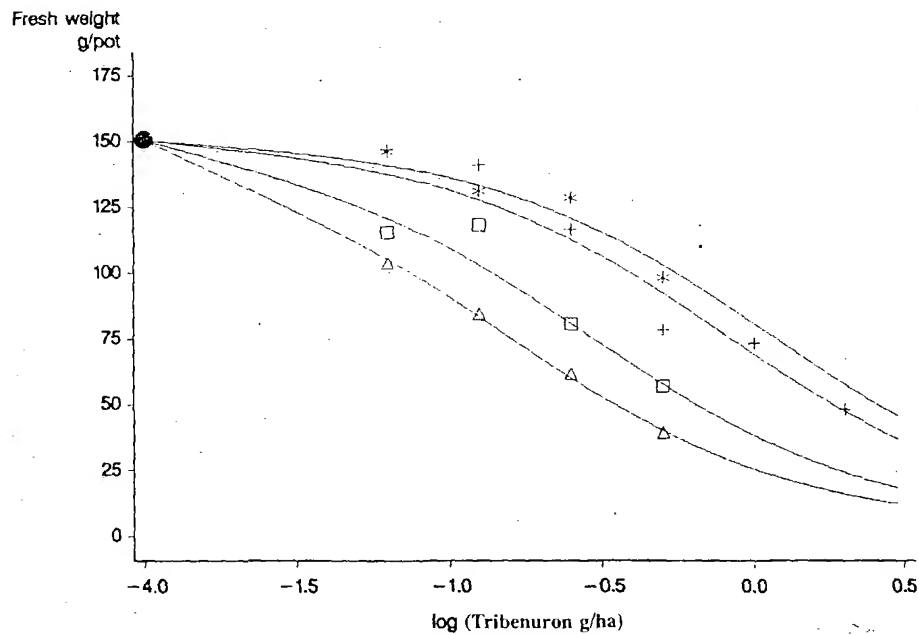


FIGURE 2. Regression of *Sinapis alba* fresh weight on DPX-L5300. (+) Without Extravon; (\*) 0.1% Extravon; (□) 0.5% Extravon; (Δ) 1% Extravon.

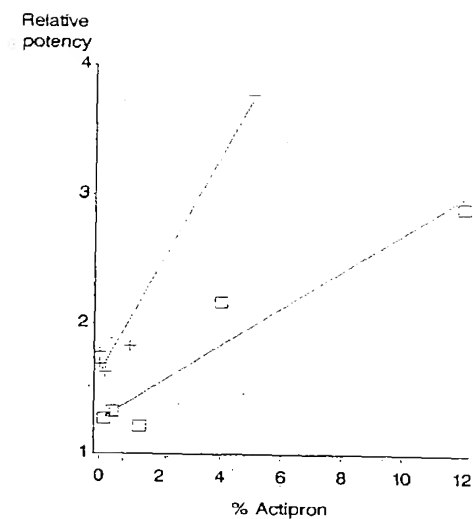


FIGURE 3. The relative potency in barley of fluazifop-butyl (□) or alloxym-sodium (+) plotted against Actipron, a 97% mineral oil with emulsifier.

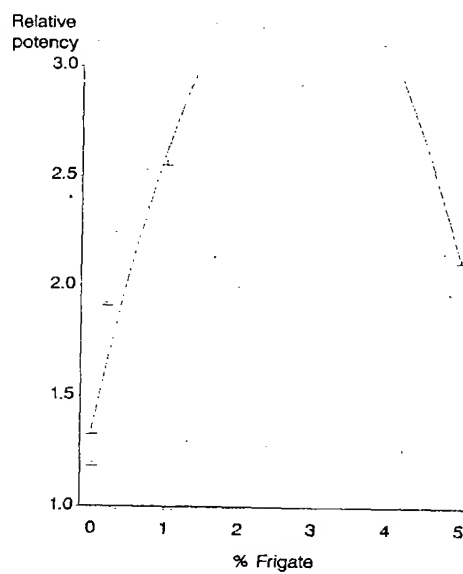


FIGURE 4. The relative potency of fluazifop-butyl in barley plotted against Frigate, a weakly cationic fatty amine ethoxylate.

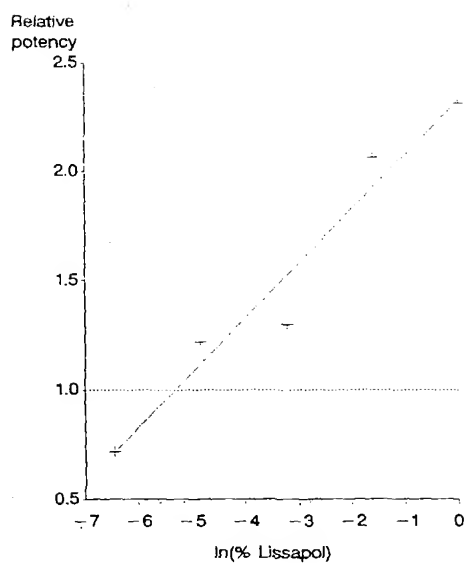


FIGURE 5. The relative potency of fluazifop-butyl in barley plotted against Lissapol, a nonionic alkyl-aryl-polyoxyethylene.

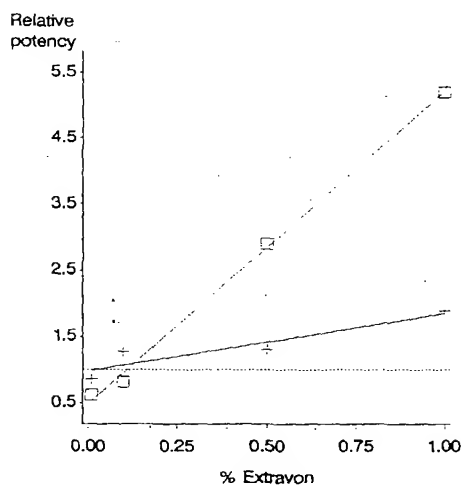


FIGURE 6. The relative potency of tribenuron, sprayed at the cotyledon stage (+) and the two-true-leaf stage (□) of *Sinapis alba* plotted against Extravon, a nonionic alkyl-aryl-polyoxyethylene.

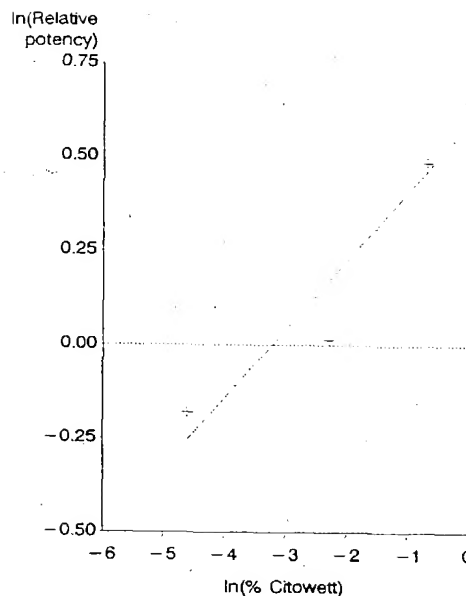


FIGURE 7. The relative potency of tribenuron in *Sinapis alba* plotted against Citowett, a nonionic alkyl-aryl-polyoxyethylene,

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## Chapter 50

**NONIONIC SURFACTANT PROPERTY EFFECTS ON  
THIFENSULFURON METHYL PERFORMANCE IN SOYBEANS**

Jerome M. Green, Philip A. Brown, David Berengut, and Michael G. King

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## ABSTRACT

Surfactant rate and properties affect thifensulfuron methyl {methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]2-thiophenecarboxylate} performance. Fourteen properties describing the physical, chemical, and surface characteristics for 300 surfactants were quantified and a statistical algorithm selected a small subset which could efficiently evaluate their importance. Two years of greenhouse and field studies show that properties which affect hydrophilic and lipophilic characteristics are most important, followed by properties such as melting point and equilibrium water content which affect the deposit on the leaf. The optimum surfactant has a medium to high number of ethylene oxides, a medium to high hydrophilic-lipophilic balance, an intermediate melting point, and a high water-holding capacity. These properties are used to select surfactants with the optimum properties.

## I. INTRODUCTION

Thifensulfuron methyl, previously known as DPX-M6316, is a postemergence sulfonyl-urea herbicide that controls broadleaf weeds in wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), corn (*Zea mays* L.), and soybeans (*Glycine max* L. Merr.) (Figure 1). It is used postemergence only because it breaks down rapidly to inert ingredients.<sup>1</sup> The type and rate of adjuvant significantly affect thifensulfuron methyl performance.<sup>5</sup> Because it has a narrow selectivity margin, the ideal surfactant will enhance weed control, but not soybean injury. To search for this surfactant, we quantified 14 properties for 300 surfactants and used statistical methodology to determine the optimum properties.

## II. MATERIAL AND METHODS

### A. SURFACTANT PROPERTY INFORMATION

We obtained quantitative information on 14 physical properties for 300 surfactants. These properties were selected because they describe the physical, chemical, and surface characteristics of surfactants. Most of the information was obtained from public sources.<sup>2,3</sup>

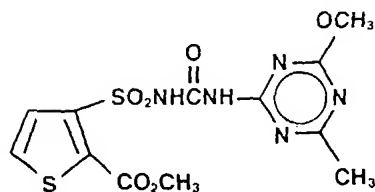
The 14 properties used in these analyses were pH, hydrophilic-lipophilic balance (HLB), moles of ethylene oxide (MEO), ionic class, melting point (MP), chemical type, water and oil solubility, static surface tension (SST), initial physical state, physical state of the deposit, equilibrium water content, spread coefficient (SC), and molecular weight (MW). The effect of dynamic surface tension is under study and will be reported.

The pH was determined in a 0.25% w/v surfactant concentration in a sulfonylurea herbicide spray solution. The HLB and MEO were from public sources or from inspection of the surfactant's chemical structure. The MP in °C was from public sources or direct measurement. Chemical type was grouped into categories representing surfactants with only carbon, hydrogen, and oxygen, with nitrogen, sulfur, phosphorous, silicone, and fluorine.

Water and oil solubility information is from public sources or direct measurement. This is grouped into categories where 0 = 0 to 1% solubility, 1 = 1 to 10%, and 2 = >10%. Surface tension (dyn/cm) represents the minimum equilibrium surface tension of an aqueous solution.

Initial physical state was categorized as gel, liquid, or solid. To simulate the physical state of the deposit on a leaf surface, we spotted a spray mixture containing a sulfonylurea herbicide and each surfactant on a glass slide. After 5 d at 81° relative humidity, we determined the physical state of the deposit with the same categories and also measured the equilibrium water content by gravimetric or Karl Fischer determination.

## Thifensulfuron Methyl



Dissociation constant:	pKa = 4.0 at 25°C
Partition coefficient: (octanol/water)	0.027 at pH 7.0
Vapor pressure	1.3 x 10 <sup>-7</sup> mm Hg at 25°C
Water solubility:	pH 4.0 24
(mg/ml at 25°C)	pH 6.0 2,400

FIGURE 1. Chemical structure and properties of thifensulfuron methyl.

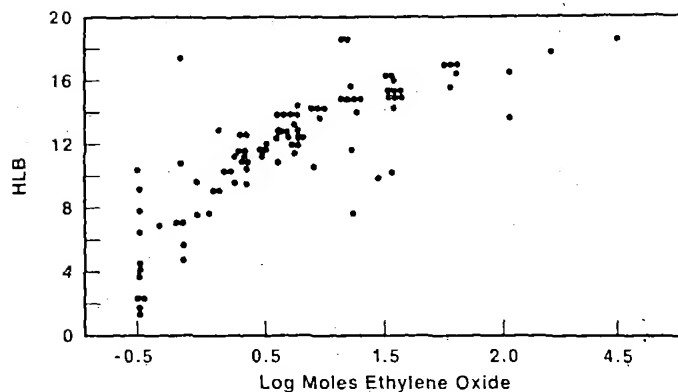


FIGURE 2. Correlation of HLB and MEO.

To simulate how the herbicide-surfactant spray droplet spreads on the leaf surface, we determined the SC as the ratio of the leaf area covered by a 1- $\mu$ l droplet of spray solution and the area covered by a 1- $\mu$ l droplet of pure water.

## B. STATISTICAL APPROACH

We used these 14 properties as independent variables in statistical procedures to identify those properties which are important for biological activity. We transformed these properties, where necessary, so their distributions were as close to normal as possible. Logarithms were used for SC, MEO, and MW and square roots for SST, MP, and equilibrium water content.

Because more surfactants were available than could be readily tested, we selected a subset which would yield as much information as possible. Prior to selecting the subset, we examined correlations among properties. To effectively use the subset methodology, we developed a quadratic model with a reduced number of properties by eliminating properties that were highly correlated with others. Some properties, such as MEO and HLB, were highly correlated (Figure 2); others, such as surface tension and equilibrium water content,

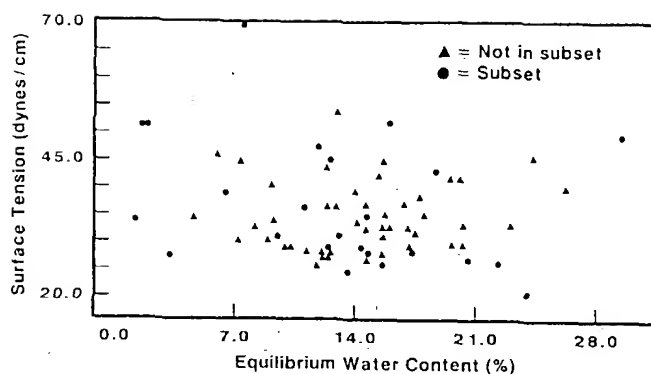


FIGURE 3. Scatter plot of surface tension vs. equilibrium water content.

TABLE 1  
Field Performance of 8 g/ha Thifensulfuron  
Methyl

Plant species	Without surfactant		With surfactant	
	%	SD	%	SD
Soybean	4	(8)	13	(14)
Velvetleaf	77	(22)	87	(11)
Common lambsquarters	42	(34)	83	(22)
Common cocklebur	72	(24)	83	(13)

were not (Figure 3). The final model had seven properties, each with a linear and quadratic term.

The selection was done with the aid of ECHIP<sup>®</sup> (Expert in a Chip, Inc.; Hockessin, DE), a PC-based software package for the statistical design and analysis of experiments. Using the algorithmic (D-optimal) design feature and the quadratic model developed earlier, we selected a subset of 21 surfactants which would minimize the maximum prediction variance over the property space.<sup>4,6,8</sup> Four additional surfactants (commercial standards) were forced into the subset to obtain the final 25.

### C. BIOLOGICAL EVALUATIONS

Table 1 summarizes 200 field tests which compare 8 g/ha thifensulfuron with and without surfactant or crop oil concentrate. All results are included regardless of the type of surfactant or crop oil concentrate and the weed or crop growth stage.

All other field and greenhouse studies were done at Newark, DE. Plants were sprayed 2 to 4 weeks after planting and evaluated 2 to 3 weeks later. Field treatments were visually evaluated. Greenhouse plants were weighed and converted to percent soybean injury or weed control. Surfactants were compared at 0.25% w/v.

Surfactants were field tested 2 years in a completely randomized block design with four replications and greenhouse tested at approximately the same time in a completely randomized design with six replications. Surfactant ranking and biology correlated about 80% between years and between the field and greenhouse. The thifensulfuron methyl rate was 2 or 4 g/ha on weeds and 8 or 16 g/ha on soybeans. The selectivity margin was determined by subtracting all soybean injury results from all weed control results.



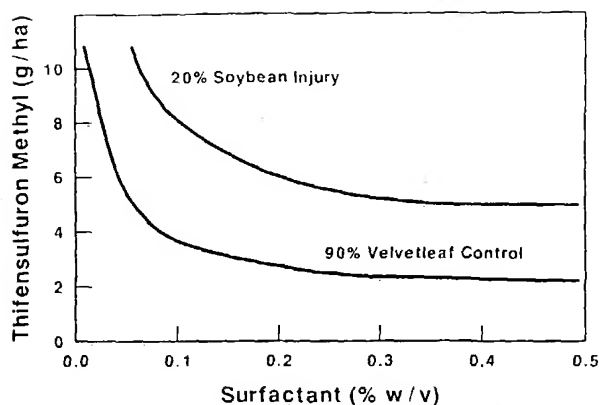


FIGURE 4. Contour plot showing the interaction of thifensulfuron methyl and surfactant Tergitol® TMN6 on velvetleaf and soybeans.

TABLE 2  
Surfactant Ranking of 2 g/ha Thifensulfuron Methyl on Common Cocklebur

Surfactant	Control (%)	Surfactant	Control (%)	Surfactant	Control (%)
Tween® 65	57	Tween® 40	45	Pluronic® F68	40
Renex® 30	54	Zonyl® FSN	45	G1683	31
Tergitol® TNM6	53	Triton® X-100	44	Surfynol® 440	30
Tergitol® 15S9	52	Igepal® RC520	43	Span® 85	16
Pluronic® L35	51	Igepal® RC630	43	Surfynol® 82	15
Tergitol® 15S7	50	Renex® 36	42	Span® 65	13
Tween® 20	48	Span® 20	42	Span® 40	11
Brij® 78	47	Emulphogene® BC610	40	No surfactant	18
Tergitol® 24L92	45	Merpel® SH	40		

### III. RESULTS AND DISCUSSION

#### A. FIELD PERFORMANCE

Thifensulfuron is very active on velvetleaf (*Abutilon theophrasti* Medicus), common lambsquarters (*Chenopodium album* L.), and common cocklebur (*Xanthium strumarium* L.), but has a narrow selectivity margin on soybeans (Table 1). Surfactants and crop oils enhance its activity on both weeds and soybeans. To increase this selectivity margin, we evaluated a wide range of surfactant rates and properties.

#### B. EFFECT OF SURFACTANT RATE

First we changed the surfactant rate (Figure 4). In 2 years of greenhouse and field testing, lowering the surfactant rate lowered thifensulfuron methyl's weed activity and soybean injury in an approximately parallel fashion. Surfactant allows thifensulfuron methyl to be used at lower rates.

#### C. SURFACTANT PROPERTY EFFECTS ON COMMON COCKLEBUR

We compared the subset's 25 surfactants on soybean, velvetleaf, and common cocklebur. Table 2 shows representative results from a greenhouse test on common cocklebur with 2 g/ha thifensulfuron methyl.

TABLE 3  
Single-Term Model Ranking for  
Thifensulfuron Methyl on Common  
Cocklebur

Model terms	Adjusted R <sup>2</sup>
MEO	0.54
HLB	0.43
Melting point	0.33
Water solubility	0.25
SST	0.10
Equilibrium water content	0.06
Physical state	0.04
pH	0.01
MW	0.00
Oil solubility	-0.02
Spread coefficient	-0.02

Note: MEO, moles of ethylene oxide; HLB, hydrophilic-lipophilic balance; SST, static surface tension; MW, molecular weight.

TABLE 4  
Two-Term Model Ranking for  
Thifensulfuron Methyl on  
Common Cocklebur

Model terms		Adjusted R <sup>2</sup>
MEO	MP	0.73
HLB	MP	0.67
MEO	MEO <sup>2</sup>	0.63
MEO	SST	0.61
MEO	Oil Sol.	0.61
HLB	HLB <sup>2</sup>	0.59

Note: MEO, moles of ethylene oxide; HLB, hydrophilic-lipophilic balance; MP, melting point; SST, static surface tension.

Control varied with surfactant from 11 to 57%. A single MEO or HLB term explained close to 50% of the biological variation (Table 3). MP and water solubility were also important, but none of the other properties alone explained more than 10% of the biology.

The best two-term models (Table 4) were combinations of MEO or HLB with MP and MEO or HLB with a quadratic term. These models gave high R<sup>2</sup> values. The importance of a quadratic term indicates an optimum level for MEO and HLB. This has also been shown with other herbicides.<sup>7</sup>

In the final model, we could support three property terms. In this case, MEO or HLB was the most important property. The next most important term was MP and the third was oil solubility. The best overall model to explain common cocklebur activity with these properties was this three-property model. Note that all terms are significant at 0.1 level; adjusted R<sup>2</sup> equals 0.92.

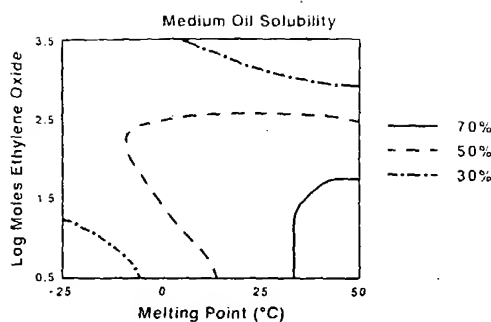


FIGURE 5. The effect of surfactant physical properties on the common cocklebur activity of 2 g/ha thifensulfuron methyl.

$$\begin{aligned}
 \% \text{ Control} = & 27.88 + 14.7 \text{ MEO} - 2.7 \text{ MEO}^2 \\
 & + 0.7 \text{ MP} \\
 & + 8.5 \text{ oil solubility} \\
 & - 0.3 \text{ MEO} \cdot \text{MP} \\
 & - 3.2 \text{ MEO} \cdot \text{oil solubility}
 \end{aligned} \quad (1)$$

Figure 5 plots this model. Changing surfactant properties greatly enhances thifensulfuron methyl activity on common cocklebur.

#### D. SURFACTANT PROPERTY EFFECTS ON SELECTIVITY MARGIN

To evaluate overall thifensulfuron methyl performance, we created a quantitative measure for the margin of selectivity by summing all weed control data and subtracting all crop injury data. We analyzed these data in a manner analogous to that described in Section III.C for common cocklebur. Figure 6 plots the final model.

These results indicate that maximum selectivity results from surfactants with a medium to high MEO, a medium to high HLB, an intermediate MP, and a high equilibrium water content. Thifensulfuron methyl selectivity depends mostly on properties that affect the hydrophilic and lipophilic characteristics, but other factors such as MP and equilibrium water content that affect the physical form of the deposit are also important.

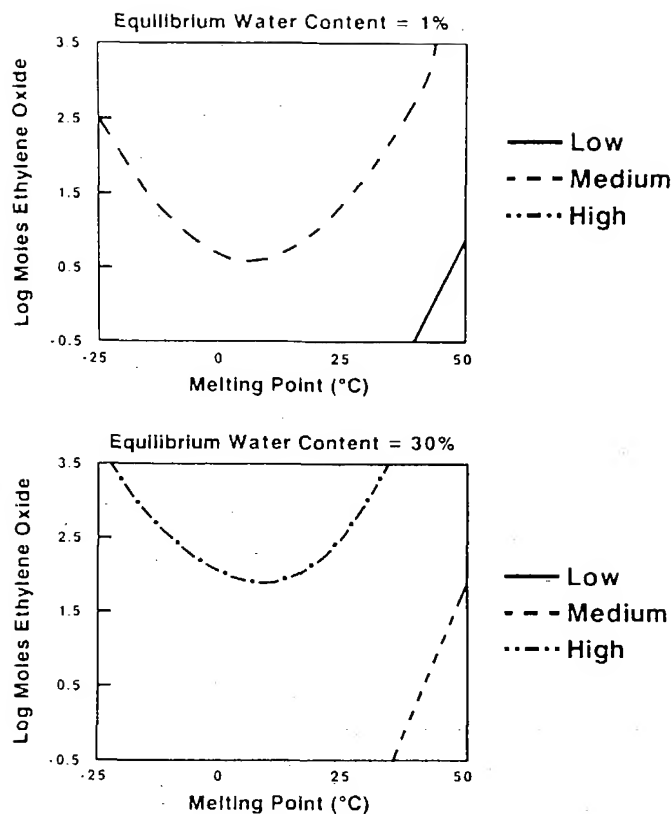


FIGURE 6. The effect of surfactant physical properties on the selectivity margin of thifensulfuron methyl.

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## Chapter 51

**THE USE OF DOWFAX<sup>TM</sup> SURFACTANTS TO IMPROVE THE  
EFFICACY OF HERBICIDE PRODUCTS**

Smallwood Holoman, Jr. and Lisa B. Quencer

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## I. ABSTRACT

DOWFAX<sup>®</sup> (Trademark of Dow Chemical Co.) surfactants are used as wetting agents and dispersants for pesticide active ingredients in agricultural products. Independent greenhouse and field studies were conducted to determine if the addition of DOWFAX surfactants would enhance the biological activity of certain commercial herbicide products when used as a tank-mix adjuvant. Test results using commercial formulations of atrazine, acifluorfen (Blazer<sup>®</sup>, Rohm and Haas Co.), 2,4-D, glyphosate (Rodeo<sup>®</sup>, Monsanto Agricultural Co.), and fluazifop-butyl (Fusilade<sup>®</sup>, ICI Americas, Inc.), herbicides show increased control of certain broadleaf weeds and grasses up to 80% over that of the standard treatment. Also, little to no injury was observed to beneficial host plants such as corn (*Zea mays* L.) and soybean (*Glycine max* (L.) Merr.).

## I. INTRODUCTION

Surfactants are known by many names, including surface-active agent, detergent, emulsifier, dispersant, wetter, wetting agent, spreader, sticker, activator, and adjuvant. Depending on the industry, some of these names are used interchangeably. The agricultural industry, in particular, uses all of these names. The terms "adjuvant" and "surfactant" will be used synonymously in this study.

Surfactants function in many ways when used in agricultural products. They may reduce tension and produce better coverage on the leaves by herbicide, remove air pockets between the spray and leaf surface, and solubilize nonpolar plant substances such as the waxy cuticle or lipid portions of the cell wall to alter both leaf cell and plasma membranes. All of these factors contribute to increased efficacy by causing the applied herbicides to penetrate more readily and to spread through the plant. Thus, surfactants increase the availability of herbicides at the site of action and enhance the toxicity to weeds.

In general, adjuvants include surfactants and inorganic salts added to the formulated or unformulated herbicides in order to handle the spray in convenient or economical ways and to assist or enhance herbicidal activity for better weed control.

Alkylated diphenyl oxide disulfonates are a family of highly anionic, surface-active agents sold under the trademark DOWFAX surfactants. Their commercial utility is based on unusually high solubility, excellent stability, coupling ability, and surface activity in concentrated aqueous solutions of acids, alkalis, and salts. There are presently eight commercial products that differ primarily as a result of alkyl chain length (C6 linear, C10 linear, C12 branched, and C16 linear) and acidity ( $\text{Na}^+$  or  $\text{H}^+$  salt form). Different alkyl hydrophobes can be attached to the diphenyl oxide backbone, and variations in the degree of sulfonation and alkylation and different salts can be produced.

DOWFAX surfactants have had wide acceptance in the formulation of agricultural chemicals since the mid 1960s.<sup>1</sup> DOWFAX 3B2 (C10), 2A1 (C12), and 8390 (C16) surfactants meet EPA regulation CFR 40 180.1001 (c) when used in agricultural products "applied to growing crops". As inert ingredients, DOWFAX surfactants are the preferred surfactants for use in concentrated aqueous pesticides such as monosodium methanearsonate (MSMA), disodium methanearsonate (DSMA), and other arsenicals. In addition to water-soluble arsenicals, DOWFAX surfactants find use in other pesticidal chemicals and formulation types, such as paraquat, 2,2 dichloropropionic acid, dinitro ortho-secondary butyl phenols, 1-naphthyl methylcarbamate (Sevin<sup>®</sup>, Rhône-Poulenc Mg. Co., Paris), and 1,2,3,6-tetrahydro-N-(trichloromethylthio)phthalimide (Captan<sup>®</sup>, ICI Americas, Inc., Wilmington, DE) flowable and wettable powder.

Recently, a comparative evaluation of the efficacy-enhancing properties of several surfactants, including DOWFAX surfactants, with triclopyr (GARLON<sup>®</sup>, Dow Chemical Co.)

### Chart 1 Phase I.

Adjuvants	
DOWFAX 3B0 surfactant	
DOWFAX 3B2 surfactant	
DOWFAX 2A0 surfactant	
DOWFAX 2A1 surfactant	
DOWFAX 3B-monoethanolamine (MEA) surfactant	
DOWFAX 3B-monoisopropylamine (MIPA) surfactant	
DOWFAX 3B-triethylamine (TEA) surfactant	
DOWFAX 3B-triisopropanolamine (TIPA) surfactant	
DOWFAX 2A-MIPA surfactant	
DOWFAX 3B2 (93:7 monoalkyl-to-dialkyl ratio) surfactant	
DOWFAX 3B-MIPA (93:7) surfactant	
XDS 8292.00 experimental surfactant	
X-77	
Rate	
All adjuvants used at 0.25, 0.125, 0.06, and 0% (v/v)	
Herbicides	
Blazer 2L	0.07, 0.28 kg a.i. ha <sup>-1</sup>
Rodeo 5.6	0.94, 1.88 kg a.i. ha <sup>-1</sup>
Plant Spectra	
Fall panicum, annual morningglory, and nutsedge	
Replications	
Four randomized pots	

2,4-D amine herbicide mixture on turf was conducted. Results of this trial indicated that the diethanolamine (DEA) salts of DOWFAX 3B0 and 8390 surfactants enhanced the control of turf weeds as well as, and in some cases, better than their standard treatment. This work prompted the evaluation of other amine salts of DOWFAX surfactants to determine if they, too, would increase or enhance the efficacy of certain herbicides against grass and broadleaf weeds.

An independent agricultural consultant and management firm, American Agricultural Services, Inc., of Cary, NC, was contracted to perform greenhouse and field evaluations using five commercial herbicide products tank mixed with 12 commercial and developmental DOWFAX surfactant products and three commercial agricultural adjuvants. The results of this comparative evaluation suggest that certain amine salts of DOWFAX 2A0 and 3B0 surfactants do enhance the biological effectiveness of herbicides without injury to beneficial crops such as corn and soybean. When the activity of DOWFAX surfactants was compared to the activity of the major commercial activity of the major commercial agricultural adjuvants, DOWFAX surfactants proved to be equal to or better than the comparative adjuvants in most cases.

This chapter will review the condition and method under which this study was done and the results.

## II. METHODS AND CONDITION OF STUDY

### A. GREENHOUSE

For Phase I of this study, a broad screen was done using twelve DOWFAX surfactants and one commercial adjuvant, as noted in Chart 1. Fall panicum (*Panicum dichotomiflorum*), annual morningglory (*Ipomoea* spp.), and nutsedge (*Cyperus* spp.) were used as plant spectra, with applications to four replicates.

During Phase II of the greenhouse study, two developmental DOWFAX surfactants identified from phase I and two commercial adjuvants were evaluated further in tank mixtures

### Chart 2 Phase II.

#### Adjuvants

DOWFAX 2A-MIPA surfactant

DOWFAX 3B-MEA surfactant

X-77

Agri-dex COC

#### Rate

All adjuvants were used at 0.25% (v/v)

#### Herbicides

Blazer 2L 0.6, 1.1 kg a.i. ha<sup>-1</sup>

Rodeo 5.6 0.9, 1.9 kg a.i. ha<sup>-1</sup>

2,3-D (dimethylamine) 0.3, 1.1 kg a.i. ha<sup>-1</sup>

Fusilade 4E 0.13, 0.6 kg a.i. ha<sup>-1</sup>

Atrazine 4L 1.7, 3.4 kg a.i. ha<sup>-1</sup>

#### Plant Spectra

Soybean, morningglory, crabgrass, nutsedge, and corn (when appropriate)

#### Replications

Four randomized pots

with five herbicide products (Chart 2). Plant spectra in this test included morningglory, crabgrass (*Digitaria* spp.), soybean, nutsedge, and corn (as appropriate).

The plants used in these studies were purposely grown in an environment with limited waterings and under extreme heat to produce "stressed" grasses and broadleaf weeds. This condition produces plant foliage with a waxy cuticle (highly hydrophobic) whose barrier is more resistant to herbicide sprays, thus reducing the penetration of the herbicide into cellular targets. This represents a "worst-case" situation which challenges the effectiveness of not only the adjuvant, but also the herbicide itself.

Sprayer applications were made using a CO<sub>2</sub> backpack sprayer with a flat fan spray tip (TeeJET 8004), pressurized to 207 kPa, and applied to 282 l ha<sup>-1</sup> total spray volume (TSV). The broadcast spray technique was used to apply all treatments.

Each plant species in each surfactant/herbicide treatment was visually rated on a scale of 0 (no control or injury) to 100 (complete control or injury). Each species was treated 7 and 14 d after application. The 14-d results are presented in this report.

### B. FIELD TRIAL

At the end of the greenhouse evaluation, four DOWFAX surfactants along with two commercial adjuvants were selected for further testing with two herbicide products under actual field application conditions. The specific adjuvants and herbicides used and the application conditions are outlined in Chart 3.

## III. RESULTS

Summaries of the results, categorized by the type of study (greenhouse or field) and the herbicide used, are assembled in Tables 1 through 17.

### A. GREENHOUSE

#### 1. Surfactant Phytotoxicity Evaluation (Table 1)

All 12 DOWFAX surfactants were sprayed on the plant spectra to be used in the greenhouse study. The results indicated that the surfactants do not contribute to the phytotoxicity of grasses, broadleaf weeds, or host plants, such as corn and soybean, when used alone.

### Chart 3 Field Trial.

#### Adjuvants

DOWFAX 3B2 surfactant  
DOWFAX 3B-MEA surfactant  
DOWFAX 3B-MIPA surfactant  
DOWFAX 3B-MIPA (93:7) surfactant  
APSA-80  
X-77

#### Rate

All adjuvants were used at 0.25% (v/v)

#### Herbicides

Blazer 2L 0.6, 1.1 kg a.i. ha<sup>-1</sup>  
Rodeo 5.6 0.9, 1.9 kg a.i. ha<sup>-1</sup>

#### Plant Spectra

Soybean, prickly sida, pigweed, annual grasses, and morningglory

#### Replications

Four randomized plots

#### Application Conditions

375 l ha<sup>-1</sup> TSV using a TeeJET 8004 nozzle at 279 kPa  
Soil temperature, 29°C; soil moisture, good  
Air temperature, 36°C; relative humidity, 70%  
Wind speed, 3.2 km h<sup>-1</sup>  
Applied with CO<sub>2</sub> backpack sprayer at @ 4.8 km h<sup>-1</sup> traverse  
Plot size 3.6 × 12 m

**TABLE 1**  
**Greenhouse Study: Surfactant Phytotoxicity Evaluation**

Treatments	Soybean (v/v)	Percent injury rate (% v/v)			
		Morningglory	Nutsedge	Crabgrass	Corn
DOWFAX 3B0 surfactant	0.25	2.0	0.0	3.0	0.0
DOWFAX 3B2 surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 2A0 surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 2A1 surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 3B MIPA <sup>a</sup> surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 2A MIPA surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 3B MEA <sup>b</sup> surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 3B TEA <sup>c</sup> surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 3B TIPA <sup>d</sup> surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX XDS 8292 surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 3B2 (93:7) surfactant	0.25	0.0	0.0	0.0	0.0
DOWFAX 3B MIPA (93:7) surfactant	0.25	0.0	0.0	0.0	0.0

<sup>a</sup> Monoisopropylamine.

<sup>b</sup> Monoethanolamine.

<sup>c</sup> Triethylamine.

<sup>d</sup> Triisopropanolamine.

## 2. Blazer® 2L Herbicide (Tables 2 and 3)

At the low rate of 0.6 kg active ingredient (a.i.) per hectare, the addition of DOWFAX surfactants did not improve the activity of Blazer® 2L herbicide (trademark of Rohm and Haas) against morningglory. Only 30% control was observed when using Blazer 2L alone (control standard) or in combination with the DOWFAX surfactant adjuvants. The addition of X-77 (Valent U.S.A. Corp., Walnut Creek, CO) increased the efficacy of the herbicide

TABLE 2  
Greenhouse Study: Blazer 2L at 0.6 kg a.i. ha<sup>-1</sup> and  
Adjuvants at 0.25% (v/v)

Treatment	Percent control	
	Morningglory	Soybean
Blazer 2L	30	0
+ DOWFAX 2A-MIPA surfactant	30	0
+ DOWFAX 3B-MEA surfactant	30	0
+ X-77	100	100

TABLE 3  
Greenhouse Study: Blazer 2L at 1.1 kg a.i. ha<sup>-1</sup> and  
Adjuvants at 0.25% (v/v)

Treatment	Percent control	
	Morningglory	Soybean
Blazer 2L	40	0
+ DOWFAX 2A-MIPA surfactant	60	0
+ DOWFAX 3B-MEA surfactant	70	0
+ X-77	100	60

TABLE 4  
Greenhouse Study: Rodeo 5.6 at 0.9 kg a.i. ha<sup>-1</sup> and  
Adjuvants at 0.25% (v/v)

Treatment	Percent control		
	Morningglory	Nutsedge	Crabgrass
Rodeo 5.6	50	43	95
+ DOWFAX 3B0 surfactant	40	36	93
+ DOWFAX 3B-MIPA surfactant	46	50	53
+ DOWFAX 3B-TEA surfactant	23	43	95
+ DOWFAX 3B-TIPA surfactant	23	26	100
+ DOWFAX 3B-MIPA (93:7) surfactant	70	90	100
+ X-77	23	80	100

to 100% control of morningglory. However, the data also showed that this same treatment with X-77 was quite injurious to the host plant, with 100% kill of the soybeans. The selectivity of the herbicide against the weeds was lost with the X-77 treatment.

At the higher rate of 1.1 kg a.i. ha<sup>-1</sup>, both DOWFAX 2A-monoisopropylamine (MIPA) and 3B-monoethanolamine (MEA) surfactant enhanced the herbicide's activity against morningglory, with up to a 75% increase in control without injury to soybean. Sprays containing X-77 again achieved excellent control of morningglory but caused excessive damage to soybean, with 60% of the plants killed.

### 3. Rodeo® 5.6 Herbicide (Tables 4 and 5)

This adjuvant screen identified a DOWFAX 3B-MIPA surfactant salt having a high monoalkylate-to-dialkylate ratio of 93:7 and DOWFAX 3B-triisopropanolamine (TIPA) surfactant as the surfactants of choice for use with Rodeo (trademark of Monsanto) herbicide at 0.94 kg and 1.9 kg a.i. ha<sup>-1</sup> applications. Control of morningglory, nutsedge, and crabgrass



TABLE 5  
Greenhouse Study: Rodeo 5.6 at 1.9 kg a.i. ha<sup>-1</sup> and  
Adjuvants at 0.25% (v/v)

Treatment	Percent control		
	Morningglory	Nutsedge	Crabgrass
Rodeo 5.6	50	40	95
+ DOWFAX 3B0 surfactant	36	95	100
+ DOWFAX 3B-MIPA surfactant	33	95	100
+ DOWFAX 3B-TEA surfactant	33	100	96
+ DOWFAX 3B-TIPA surfactant	60	100	100
+ DOWFAX 3B-MIPA (93:7) surfactant	70	100	100
+ X-77	36	40	78

TABLE 6  
Greenhouse Study: Atrazine 4L at 1.7 kg a.i. ha<sup>-1</sup>, DOWFAX at 0.25% (v/v)  
and Agridex COC at 2.3 l ha<sup>-1</sup>

Treatment	Percent control			
	Morningglory	Crabgrass	Nutsedge	Corn
Atrazine 4L	60	50	0	10
+ DOWFAX 2A-MIPA surfactant	95	30	10	0
+ DOWFAX 3B-MEA surfactant	70	30	10	0
+ Agridex COC	90	60	0	0

TABLE 7  
Greenhouse Study: Atrazine 4L at 3.4 kg a.i. ha<sup>-1</sup>, DOWFAX at  
0.25% (v/v), and Agridex COC at 2.3 l ha<sup>-1</sup>

Treatment	Percent control			
	Morningglory	Crabgrass	Nutsedge	Corn
Atrazine 4L	90	40	10	0
+ DOWFAX 2A-MIPA surfactant	80	50	10	10
+ DOWFAX 3B-MEA surfactant	50	30	20	0
+ Agridex COC	60	60	0	0

at 70, 90, and 100%, respectively, was obtained at the low application rate with the MIPA salt. These values represented a 40, 109, and 5% enhancement in herbicide activity over that of the herbicide when used alone; 80, 100, and 100% control of the same weeds, respectively, were obtained with the TIPA salt at the higher herbicidal rate. This represents a 60, 150, and 5% increase in control of the weeds.

The commercial adjuvant X-77 showed no enhancement in the control of crabgrass at the low rate of herbicide. No increase in control of any weeds was observed at the high application rate.

Since Rodeo is a broad-spectrum herbicide designed to kill all vegetation, no selectivity study was conducted.

#### 4. Atrazine 4L Herbicide (Tables 6 and 7)

At the low rate of atrazine (1.7 kg a.i. ha<sup>-1</sup>), both DOWFAX surfactants and Agridex® COC (Helena Chemical Co.) showed improved activity against morningglory (15 to 68%) with no injury to corn. No improvement in activity was seen at the higher application rate of atrazine (3.4 kg a.i. ha<sup>-1</sup>) with either DOWFAX surfactant or the commercial adjuvant.

TABLE 8  
Greenhouse Study: 2,4-D (Dimethylamine) at 0.3 kg a.i. ha<sup>-1</sup> and  
Adjuvants at 0.25% (v/v)

Treatment	Percent control		
	Morningglory	Nutsedge	Corn
2,4-D (amine)	95	70	30
+ DOWFAX 2A-MIPA surfactant	100	40	0
+ DOWFAX 3B-MEA surfactant	90	70	0

TABLE 9  
Greenhouse Study: 2,4-D (Dimethylamine) at 1.1 kg a.i. ha<sup>-1</sup> and  
Adjuvants at 0.25% (v/v)

Treatment	Percent control		
	Morningglory	Nutsedge	Corn
2,4-D (amine)	100	40	10
+ DOWFAX 2A-MIPA surfactant	90	50	0
+ DOWFAX 3B-MEA surfactant	95	70	10

TABLE 10  
Greenhouse Study: Fusilade 4E at 0.13 kg a.i. ha<sup>-1</sup>  
and Adjuvants at 0.25% (v/v)

Treatment	Percent control	
	Crabgrass	Soybean
Fusilade 4E	10	0
+ DOWFAX 2A-MIPA surfactant	40	0
+ DOWFAX 3B-MEA surfactant	40	0
+ X-77	30	0

TABLE 11  
Greenhouse Study: Fusilade 4E at 0.3 kg a.i. ha<sup>-1</sup>  
and Adjuvants at 0.25% (v/v)

Treatment	Percent control	
	Crabgrass	Soybean
Fusilade 4E	50	0
+ DOWFAX 2A-MIPA surfactant	70	0
+ DOWFAX 3B-MEA surfactant	40	0
+ X-77	30	0

##### 5. 2,4-D Herbicide (Tables 8 and 9)

The rates of herbicide used in these experiments were too high to discern the contribution offered by the adjuvants. However, it should be noted that the treatments containing DOWFAX surfactants, appear to safen the herbicidal effect against corn, as seen in Table 8.

##### 6. Fusilade® 4E Herbicide (Tables 10 and 11)

Enhanced biological activity, greater than 100%, was achieved with adjuvants DOWFAX 2A-monoethanolamine (MEA) and 3B-MEA surfactants and X-77 when used with the lower

TABLE 12  
Field Study: Adjuvants at 0.25% (v/v) of a 375 l ha<sup>-1</sup> Total Spray Volume

Treatment	% Injury				
	Soybean	Prickly sida	Pigweed	Annual grasses	Annual morningglory
DOWFAX 3B2 surfactant	0	0	0	0	0
DOWFAX 3B-MEA surfactant	0	0	0	0	0
DOWFAX 3B-MIPA surfactant	0	0	0	0	0
DOWFAX 3B-MIPA (93:7) surfactant	0	0	0	0	0
X-77	0	0	0	0	0
APSA-80	0	0	0	0	0

TABLE 13  
Field Study: Blazer 2L at 0.6 kg a.i. ha<sup>-1</sup> and Adjuvants at 0.25% (v/v)

Treatment	Percent control				
	Soybean	Prickly sida	Pigweed	Annual grasses	Annual morningglory
Blazer 2L	0	0	0	0	0
+ DOWFAX 3B2 surfactant	0	0	0	0	0
+ DOWFAX 3B-MEA surfactant	5	25	25	0	50
+ DOWFAX 3B-MIPA surfactant	8	0	0	15	0
+ DOWFAX 3B-MIPA (93:7) surfactant	0	0	85	0	65
+ X-77	0	0	20	0	50
+ APSA-80	5	0	90	0	100

rate of Fusilade 4E (0.13 kg a.i. ha<sup>-1</sup>), and only DOWFAX 2A-MEA surfactant offered increased activity (40%) when used with the higher application rate (0.6 kg a.i. ha<sup>-1</sup>). The commercial standard X-77 and DOWFAX 3B-MEA surfactant showed no enhancement at the high rate. It should be noted that excellent selectivity was observed with all treatments. No injury to soybean was observed. Fusilade is the trademark of ICI Americas, Inc.

## B. FIELD EVALUATIONS

### 1. Surfactant Phytotoxicity Evaluation (Table 12)

The DOWFAX surfactants and commercial adjuvants used in the field test were observed for their potential damage to plant foliage when used without herbicides. The data showed that none of the adjuvants tested contributed to the phytotoxicity of any of the weeds or the host crop.

### 2. Blazer 2L Herbicide (Tables 13 and 14)

Enhanced biological activity was observed with Blazer 2L at both the low and high application rates (0.6 and 1.1 kg a.i. ha<sup>-1</sup>, respectively), with control of targeted weeds up to 100%. Blazer 2L, when used alone, offered no control of weeds. Control adjuvant APSA-80® (Amway) showed good control of weeds, up to 95%. Little enhancement was observed with the addition of X-77 (20% control). All treatments were relatively safe to soybean, with only 5% injury.

### 3. Rodeo 5.6 Herbicide (Tables 15 and 16)

Even though the rate of application of herbicide was too high (as evidenced by the 100% control of all weeds when the herbicide was applied alone at the high rate), the contributions

TABLE 14  
Field Study: Blazer 2L at 1.1 kg a.i. ha<sup>-1</sup> and Adjuvants at 0.25% (v/v)

Treatment	Percent control				
	Soybean	Prickly sida	Pigweed	Annual grasses	Annual morningglory
Blazer 2L	0	0	0	0	0
+ DOWFAX 3B2 surfactant	5	0	0	0	0
+ DOWFAX 3B-MEA surfactant	5	0	70	0	80
+ DOWFAX 3B-MIPA surfactant	5	0	100	0	100
+ DOWFAX 3B-MIPA (93:7) surfactant	5	0	80	0	100
+ X-77	5	0	0	0	20
+ APSA-80	5	0	90	0	95

TABLE 15  
Field Study: Rodeo 5.6 at 0.9 kg a.i. ha<sup>-1</sup> and Adjuvants at 0.25% (v/v)

Treatment	Percent control				
	Soybean	Prickly sida	Pigweed	Annual grasses	Annual morningglory
Rodeo 5.6	83	88	88	88	50
+ DOWFAX 3B2 surfactant	78	88	100	73	20
+ DOWFAX 3B-MEA surfactant	81	80	100	80	100
+ DOWFAX 3B-MIPA surfactant	96	100	100	100	100
+ DOWFAX 3B-MIPA (93:7) surfactant	88	86	98	88	100
+ X-77	98	100	100	100	100
+ APSA-80	83	68	100	88	70

TABLE 16  
Field Study: Rodeo 5.6 at 1.9 kg a.i. ha<sup>-1</sup> and Adjuvants at 0.15% (v/v)

Treatment	Percent control				
	Soybean	Prickly sida	Pigweed	Annual grasses	Annual morningglory
Rodeo 5.6	100	100	100	100	100
+ DOWFAX 3B2 surfactant	100	100	100	100	100
+ DOWFAX 3B-MEA surfactant	100	100	100	100	100
+ DOWFAX 3B-MIPA surfactant	100	100	100	100	100
+ DOWFAX 3B-MIPA (93:7) surfactant	98	98	100	100	100
+ X-77	100	100	100	100	100
+ APSA-80	100	100	100	100	100

from the addition of DOWFAX 3B-MEA, 3B-MIPA, and 3B-MIPA (93/7) surfactants are discernible at the lower rate of application (0.9 kg a.i. ha<sup>-1</sup>). Increases in activity up to 14% (88 to 100% control) were observed against prickly sida (*Sida spinosa* L.), pigweed (*Amaranthus* sp.), and annual grasses, and a 100% increase (50 to 100%) was achieved against annual morningglory. The commercial adjuvant X-77 produced results similar to those of DOWFAX surfactants, while APSA-80 showed less enhancement activity. Since Rodeo-brand herbicides are nonselective products, the excessive injury to soybeans was not unexpected.

TABLE 17  
Application Economics  
for the Adjuvants Tested

	Retail cost/liter <sup>a</sup> (\$)	0.9 Liter ha <sup>-1</sup> cost <sup>b</sup> /ha <sup>-1</sup>
Agridex COC	1.32-1.84	3.70 <sup>c</sup>
APSA-80	5.26-6.58	5.55 (2.22) <sup>d</sup>
X-77	3.42-4.21	3.58
DOWFAX surfactant	3.38-4.21	3.70

<sup>a</sup> Based on local grower supply and sales stores and distributors.

<sup>b</sup> Based on 0.25% (v/v) in a total spray volume of 375 l ha<sup>-1</sup>.

<sup>c</sup> Agridex-COC at 2.3 l ha<sup>-1</sup>.

<sup>d</sup> APSA-80 recommended at 336 ml (max) ha<sup>-1</sup>.

#### IV. APPLICATION ECONOMICS

Preliminary application economics have been developed on the additional cost per hectare a farmer would realize if he used this adjuvant technology to enhance the biological action of his herbicide. Comparisons have been made between the use of DOWFAX surfactants at the experimental use level vs. that of the three commercial adjuvants used in this trial at their recommended use concentrations (Table 17).

The data suggested that the additional cost per hectare incurred for DOWFAX surfactants (\$3.70) was comparable to that of the three adjuvants tested (\$2.22 to \$3.70 per hectare).

#### V. CONCLUSIONS

DOWFAX surfactant amine salts, when used as adjuvants, enhance the biological performance of certain herbicides against both broadleaf and grassy weeds. When used with selective herbicides, DOWFAX surfactant amine salts exhibit low phytotoxicity and are beneficial to crops such as corn and soybean. Additionally, DOWFAX surfactant amine salts are cost efficient when used as adjuvants. Their cost per hectare was comparable to that of the more popular commercial adjuvants presently on the market.

To further define the efficiency of the DOWFAX surfactant amine salts and the optimum use concentrations needed for maximum activity, more greenhouse and field evaluations are needed.

#### REFERENCE

1. Woodger, S. M. and Corte, M., Herbicidal Concentration Containing Monosodium Acid Methanearsonate, U.S. Patent 3,298,820, 1967.



## Chapter 52

**EFFECTS ON BRUSH CONTROL FROM THE ADDITION OF  
ADJUVANTS TO GLYPHOSATE\***

Raj Prasad

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\* This work was completed at the Forest Pest Management Institute, Forestry Canada, Sault Ste. Marie, Ontario, while the author was on the staff there.

## ABSTRACT

A field study conducted over a period of 2 years in forest plantations in Northern Ontario demonstrated that addition of several adjuvants to commercial formulation of Vision® and Accord-CR (glyphosate) at low-volume rates (30 l/ha) did not improve efficacy significantly. It is suggested that no benefits would be gained from addition of adjuvants such as Ethokem and Triton®-XR to aerial application of Vision under forestry situations where low-volume rates of Vision are employed.

## I. INTRODUCTION

Spray adjuvants, by definition, are a class of compounds designed to modify and facilitate the effectiveness of the active ingredient.<sup>4</sup> In so doing, their addition to a pesticidal prescription reduces the cost of application and environmental burden in the forests. Although considerable research has been carried out on herbicide and adjuvant interactions with weeds in agricultural crops,<sup>4,6,11</sup> very little information is available concerning the influence of surfactants on forest weeds. Generally, forest weeds are perennial and more difficult to control than agricultural (annual) weeds. Therefore, use of adjuvants in conjunction with forest herbicides offers an opportunity for better management of weeds in forestry. To this end, extensive greenhouse and laboratory studies were carried out on the role of various adjuvants in modifying the efficacy of glyphosate on forest species.<sup>8,9</sup> Some of the promising adjuvant and herbicide combinations from these studies were tested under field conditions, and this chapter describes the effect on brush control of the addition of several adjuvants (ammonium sulfate, Enhance, Ethokem, Frigate®, LI-700, Triton-XR, and Tween-20) at different dosage and volume rates of application.

## II. MATERIALS AND METHODS

### A. FIELD PLOTS

All experiments were conducted on provincial crown (Ontario Ministry of Natural Resource) land near Constance Lake, 20 km north of Iron Bridge, Ontario. This area had undergone site preparation and planting with red pine (*Pinus resinosa* Aitk) about 3 to 5 years previously. The site consisted of flat terrain with a coarse sand/gravel substrate covered by a thin organic layer. The trial was laid out in a randomized block design with four replications of each treatment. Plot dimensions were 6 × 6 m for "high-volume" (180 l/ha) and 23 × 8 m for "low-volume" (30 l/ha) treatments. A buffer zone (2 m) was left between plots to minimize cross-contamination.

Trembling aspen (*Populus tremuloides* Michx) 2 to 3 m high was chosen as the target species because of its preponderance and uniform distribution, with a density of  $90 \pm 20$  stems per plot. For measurement of phytotoxic effects of these treatments on the crop species, three red pine trees were selected and marked in each plot.

### B. CHEMICALS

Vision (glyphosate isopropylamine salt, 356 g/l) was obtained from Monsanto Canada Ltd., Mississauga, Ontario, and contained 15% (v/v) Mon-0818 (ethoxylated tallow amine) as an adjuvant. In order to test another formulation of glyphosate, Accord-CR was also obtained from the same supplier. Accord-CR contained only 10% (v/v) Mon-0818. Two dosage rates of Vision (0.35 and 1.1 kg/ha) were investigated and, in order to compare the effect of different volume rates of application, two rates (30 and 180 l/ha) were chosen. Water, as a carrier, was obtained from nearby Constance Lake, Ontario, and was filtered

TABLE 1  
Properties of Adjuvants Used in the Experiment

Adjuvant	Rate	Property	Manufacturer
Ammonium sulfate	2.5 kg/ha	—	Fisher Chemical Co, Toronto
Enhance	0.5% (v/v)	Nonionic	Elanco Canada, Toronto
Ethokem	0.5% (v/v)	Cationic	Midkem Ltd, U.K.
Frigate	0.5% (v/v)	Nonionic	S. R. Biotech, Guelph, Ontario
LI-700	0.5% (v/v)	Nonionic	Hopkins Ltd., Co, U.S.
Triton-XR	0.5% (v/v)	Nonionic	Rohm and Haas Ltd, Ontario
Tween-20	0.5% (v/v)	Nonionic	Atkemix, Toronto

before tank-mixing with adjuvants and Vision formulations. Seven adjuvants (ammonium sulfate, Enhance, Ethokem, Frigate, LI-700, Triton-XR, and Tween-20) were supplied by the agencies listed in Table 1.

### C. TREATMENT

After screening the properties of the adjuvants in the greenhouse against three species of forest weeds — (white birch, *Betula papyrifera* L.; western alder, *Alnus rubra* L.; and trembling aspen — and three species of conifers — white spruce, *Picea glauca* (Moench-Voss); black spruce; *Picea marina* (Mill-BSP); and red pine — it was found that none of the aforementioned compounds was phytotoxic.<sup>8,9</sup> Hence, a dosage rate (0.5%, v/v) of adjuvants was selected. Treatment blocks at two high-volume rates included a control (check) plot, a plot treated with Vision alone, and plots treated with Vision in combination with one of seven different adjuvants. Treatments were applied on August 3, 1987, using a "Solo" backpack sprayer (carrier volume, 180 l/ha; pressure, 175 kPa), on a warm (28°C), sunny day.

For experiments on low volume rates (30 l/ha), an arrangement similar to the above was made, except that the vegetation was smaller (1 to 1.5 m) so that a control droplet applicator (CDA-"Herbi"<sup>TM</sup>) could be conveniently used. This atomizer operates by a gravity-feed system, and the spray can only be applied with reasonable uniformity on vegetation of less than shoulder height. For this reason, all vegetation over 1.5 m was removed several weeks prior to treatment, as were dead or dying trees. Because of the workload, only three adjuvants (Ethokem, Enhance, and Triton-XR) were applied with Vision and Accord formulations. To minimize drift, spraying was carried out just after dawn or prior to sunset. Swath widths for the "Herbi" were determined ahead of time, and swath-line markers were used to prevent overlap. Walking speed was maintained using distance markers and a stop watch. Rhodamine dye (0.02%, v/v) was added to each spray mix and Kromekote cards were laid out in plots prior to application so that uniformity of deposits could be verified.

### D. STATISTICAL ANALYSIS

For brush control assessment, the recommended Expert Committee on Weeds (ECW) method of phytotoxicity (1 to 100%) was adopted.<sup>8,9</sup> Damage was evaluated for two consecutive years, and the percentage figures were transformed to an angular scale (arcsin) according to the methods of Snedecor<sup>12</sup> before being subjected to analysis of variance. Because second-year data on phytotoxicity were more meaningful than first-year data, statistical analyses were performed on the second-year data only.

TABLE 2  
Effects of Ammonium Sulfate and Vision on Brush Control

Treatment	Rate/ha		Brush control (%)	
	kg	Water	1987	1988
Check	0	0	0	0
Ammonium sulfate	2.5	180 l	0	0
Vision	0.5	180 l	21	37
Vision + Ammonium sulfate	0.5 + 2.5	180 l	29	40
			LSD (0.05)	6

### III. RESULTS AND DISCUSSION

#### A. EFFECTS OF AMMONIUM SULFATE ON EFFICACY OF VISION

Ammonium sulfate in conjunction with glyphosate has been extensively used for control of quackgrass (*Elytrigia repens*) in agricultural crops.<sup>5,7</sup> However, data are lacking for forestry weeds. Hence, a field experiment on the effects of Vision-ammonium sulfate combination on aspen was attempted; and the data are presented in Table 2. It is apparent that ammonium sulfate per se did not cause any damage, but, when combined with Vision, it induced rapid burndown and scorching (contact toxicity) of the foliage followed by death and defoliation. Younger branches and buds also exhibited a similar quick burndown with this formulation, while Vision alone caused slow (systemic) phytotoxicity to treated foliage and stems. Probably because of this rapid burndown, the magnitude of response was greater in the first year than in the second year. Burning of foliage is likely to impede translocation of glyphosate to root zones. Some of the treated aspens recovered and flushed again in the second-year growth.

Several investigators<sup>1-3,13</sup> working with quackgrass have reported a similar result, and it is possible that ammonium sulfate operates by the same mechanism on aspen as on quackgrass. The precise mode of action of ammonium sulfate was not elucidated by these workers, but it is believed that addition of ammonium sulfate to Vision formulations facilitates the penetration of glyphosate into weed species. However, the phytotoxic effects do not persist significantly into the second year, and hence use of ammonium sulfate and Vision on forest weeds should remain questionable.

#### B. EFFECTS OF ORGANIC ADJUVANTS AND VISION AT HIGH CONCENTRATION AND HIGH VOLUME RATES

When the effects of several organic adjuvants plus Vision at 1.1 kg/180 l/ha were investigated, the aspens responded differently, in contrast to the quick activity (rapid burndown) induced by ammonium sulfate. Scorching, mottling, yellowing, and slow death of foliage followed by desiccation and browning of twigs and buds was observed. Ethokem and Triton-XR-Vision combinations caused the most severe symptoms of phytotoxicity in the first year of treatment (Table 3).

During the second year, the treated foliage and stems showed complete desiccation and death. Clearly, the effect of adjuvant-Vision combinations was more markedly visible in the second than in the first year. This is probably accounted for by slow translocation of the material into the root zone.<sup>8,9</sup> In spite of some initial treatment effects in the first year, there was no significant difference in phytotoxicity between Vision alone and adjuvant combinations in the second year. It was found that this rate (1.1 kg/ha) of Vision was rather high, since it killed 80% of the treated plants, and therefore it was difficult to measure the added effects of adjuvants. Consequently, another trial was undertaken with a low dosage

TABLE 3  
Effects of Adjuvants and Vision at High Concentration and High Volume on Brush Control

Treatment	Rate/ha		Brush control (%)	
	kg a.i.	Water	1988	1989
Check	0	0	0	0
Vision	1.1	180 l	29	82
Vision + Enhance	1.1 + 0.5% (v/v)	180 l	36	85
Vision + Ethokem	1.1 + 0.5% (v/v)	180 l	49	89
Vision + Frigate	1.1 + 0.5% (v/v)	180 l	38	91
Vision + Triton-XR	1.1 + 0.5% (v/v)	180 l	58	92
Vision + LI-700	1.1 + 0.5% (v/v)	180 l	28	80
Vision + Tween-20	1.1 + 0.5% (v/v)	180 l	35	85
			LSD (0.05)	19

TABLE 4  
Effects of Adjuvants and Vision at Low Concentration and High-Volume Rate on Brush Control

Treatment	Rate/ha		Brush control (%)	
	kg a.i.	Water	1988	1989
Check	0	0	0	0
Vision	0.30	180 l	30	24
Vision + Enhance	0.30 + 0.5% (v/v)	180 l	37	35
Vision + Ethokem	0.30 + 0.5% (v/v)	180 l	38	37
Vision + Frigate	0.30 + 0.5% (v/v)	180 l	40	39
Vision + Triton-XR	0.30 + 0.5% (v/v)	180 l	36	34
Vision + LI-700	0.30 + 0.5% (v/v)	180 l	28	25
Vision + Tween-20	0.30 + 0.5% (v/v)	180 l	41	36
			LSD (0.05)	8.6

of (0.30 kg/180 l/ha), and the plants were sprayed with and without various adjuvants in the same manner as for the high-concentration (1.1 kg/ha) experiment. From Table 4, it is evident that some adjuvants did produce positive (significant) effects at the low-response level, but the magnitude of enhancement is so small that addition of any adjuvant at that low concentration would not be economical.

### C. EFFECTS OF LOW CONCENTRATION AND LOW VOLUME RATES OF VISION PLUS ADJUVANTS

While use of high volume rates of carrier is recommended for ground-operated equipment, only smaller volume rates are used (for the sake of economy) for aerial application. Therefore, experiments were designed to test the efficacy of Vision and Accord with and without additional adjuvants on brush (aspen) species by using very low volume rates (30 l/ha). To perform these experiments, a control droplet applicator (CDA "Herbi") was employed. As can be seen from Tables 5 and 6, none of the adjuvants was effective in improving efficacy. Even Accord, which contains less adjuvant (10%, v/v) than Vision (15%, v/v), did not respond to the addition of extra adjuvants. Therefore, it is safe to assume that adequate amounts of surfactants are found in these formulations and that addition of any one of the surfactant products tested here would not enhance efficacy. Conceivably, at reduced volumes, the concentration of the adjuvants in the mixture also rises, hence addition



TABLE 5  
Effects of Adjuvants and Vision at Low Concentration Plus  
Low Volume on Brush Control

Treatment	Rate/ha		Brush control (%)	
	kg	Water	1988	1989
Check	0	0	0	0
Vision	0.35	30 l	27	37
Vision + Ethokem	0.35 + 0.5% (v/v)	30 l	24	35
Vision + Triton-XR	0.35 + 0.5% (v/v)	30 l	27	36
			LSD (0.05)	6

TABLE 6  
Effects of Adjuvants and Accord-CR at Low Concentration  
Plus Low Volume on Brush Control

Treatment	Rate/ha		Brush control (%)	
	kg a.i.	Water	1988	1989
Check	0	0	0	0
Accord-CR	0.35	30 l	23	33
Accord + Ethokem	0.35 + 0.5% (v/v)	30 l	24	37
Accord + Triton-XR	0.35 + 0.5% (v/v)	30 l	24	34
			LSD (0.05)	6

of any more adjuvant nullifies the additive effects of the treatments. Consequently, at the low-volume rate of Vision or Accord (30 l/ha) application, no further addition of the above-mentioned surfactants should be recommended. It is also of interest to note that Accord was specially formulated for the lower content of surfactant (10%, v/v), but even then, addition of Ethokem and Triton-XR did not improve efficacy.

In conclusion, these experiments with adjuvants amply demonstrate that Vision and Accord formulations of glyphosate contain sufficient amounts of surfactants and that addition of any further quantity at reduced volume rates is of no consequence. Therefore, in forest management practices where Vision is sprayed aerially, either for site preparation or conifer release, using lower volume rates (30 to 100 l/ha), there does not appear to be any need for additional surfactants to either enhance efficacy or economize the use of the active ingredient of glyphosate. Attempts to improve the efficacy of Vision at reduced dosage rates (0.30 to 1.1 kg/ha) via addition of surfactant did not produce significant results, and a small improvement (5 to 15%) in efficacy at the lowest dosage rate (0.30 kg/180 l/ha) does not warrant use of any adjuvants because the initial efficacy with Vision alone (30 to 40%) is not acceptable to forest managers. Likewise, the use of ammonium sulfate with a Vision formulation for forest weed management is also questionable. Several workers<sup>1-3,5,7,10</sup> reported beneficial effects of ammonium sulfate with a glyphosate formulation in controlling quackgrass and some forest weeds. Prasad<sup>8,9</sup> carried out a detailed greenhouse study of the effect of ammonium sulfate plus Vision formulations on three forest weeds: red alder, white birch, and aspen. While red alder and aspen did not respond to the addition of ammonium sulfate to the Vision mixture, white birch showed a positive increase in phytotoxicity. In all these weeds, a quick burndown of the foliage, young twigs, and buds were reported. Apparently, ammonium sulfate-Vision mixtures did not injure the "hardened" needles of white spruce, black spruce, or red pine in the greenhouse. Some discrepancy between greenhouse- and field-grown plants in relation to the response of ammonium sulfate plus

Vision can be explained on the grounds that greenhouse-grown plants are morphologically (cuticle and wax) different. Ammonium sulfate also affects the ionic balance and "hardness" of water used in glyphosate spraying, and it is possible that in quackgrass sprayings, the water was "harder" than that used in forest applications. Generally, the water source (carrier) in forest application is derived from a lake, where the water is "soft". Without further research, it is difficult to pinpoint the mode of action of ammonium sulfate. Finally, none of these adjuvants per se or their combination with Vision or Accord brought about any measurable damage to the conifer crop (red pine) in these field experiments.

### ACKNOWLEDGMENTS

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## Chapter 53

**REGULATING VEGETATIVE GROWTH OF DECIDUOUS FRUIT  
TREES IN THE NURSERY BY ADJUVANT-MEDIATED UPTAKE  
OF GIBBERELLIN BIOSYNTHESIS INHIBITORS APPLIED AS  
TRUNK PAINTS**

Eric A. Curry

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## ABSTRACT

Regulating the growth of fruit trees in the nursery is highly desirable. Foliar applications of triazole gibberellin biosynthesis inhibitors (GBIs) have been shown to control excessive vegetative growth of both mature, bearing trees and 1-year-old nursery-grown stock.

As an alternative to foliar applications, GBIs were applied directly to the bark of 1-year-old apple (*Malus sylvestris* Mill.), apricot (*Prunus armeniaca* L.), and cherry (*Prunus* sp.) trees using different adjuvants as carriers. Nine adjuvants were evaluated; three were found to be effective and nonphytotoxic. Results indicated stone fruit species may be more sensitive to triazole GBI trunk bark applications, but the effect was shorter lived than in pome fruit species.

## I. INTRODUCTION

Managing the vegetative growth of fruit trees — both mature, bearing trees and nursery trees — is a challenge to fruit growers throughout the world. Several different methods have been used in the past to control tree growth, including tree training, pruning, trunk scoring or girdling, size-controlling clonal rootstocks, and plant growth regulators. In the production of nursery trees, plant growth regulators have also been used to suppress apical dominance and induce the formation of lateral branches.<sup>1</sup> Since trees often become too large, a growth regulator which would regulate shoot extension would be very useful.

Paclobutrazol [(2RS,3RS)-1-(4-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl) pentan-3-ol] is one of a number of triazole derivatives that inhibit gibberellin biosynthesis.<sup>8</sup> This compound has been investigated for a number of years, with varying degrees of success, for its ability to control vegetative growth on many different crops. Factors such as species and cultivar, nutritional status, irrigation, soil type, and method of application influence the efficacy and longevity of the response.<sup>4,5,7,9,10,14,16</sup>

In the past, multiple foliar applications of paclobutrazol on young fruit trees in wet or humid fruit-growing regions of the world have been successful. Less consistent results have been obtained with this method in the more arid areas. Thus, an alternative method of application was sought which would (1) be effective irrespective of climatic conditions, (2) minimize environmental contamination from orchard spray equipment, (3) take effect in a relatively short period of time, and (4) be adaptable to mechanization. This chapter presents the results of trunk bark painting by GBIs in several different solvent carriers to effectively terminate vegetative shoot extension of young apple, cherry, and apricot trees.

## II. MATERIALS AND METHODS

### A. GREENHOUSE TRIALS

#### 1. Experiment 1

'Delicious' trees on seedling rootstock approximately 1.5 cm in diameter which had grown for one season were root pruned to approximately a 15-cm diameter rootball volume and potted in 4-l pots containing a sand:peat:vermiculite (1:1:1, v:v:v) mixture. Each tree was cut back to a height of 30 cm above the graft union. While the buds were still dormant, a solution of 0, 0.1, 0.4, 1.0, or 4.0% paclobutrazol in trimethylnonylpolyethoxyethanol (Surfactant WK®, E. I. du Pont E. Nemours & Co., Inc.) was painted with a small brush on the trunks to a height three times the diameter of the trunk, beginning about 10 cm above the graft union. Solutions were applied sparingly to avoid soil contamination. There were six trees per treatment replication in a completely randomized design. Within 2 weeks after the buds had begun growing, all shoots except the strongest shoot closest to the heading cut were removed. The remaining shoot was measured every 5 d for 8 weeks.

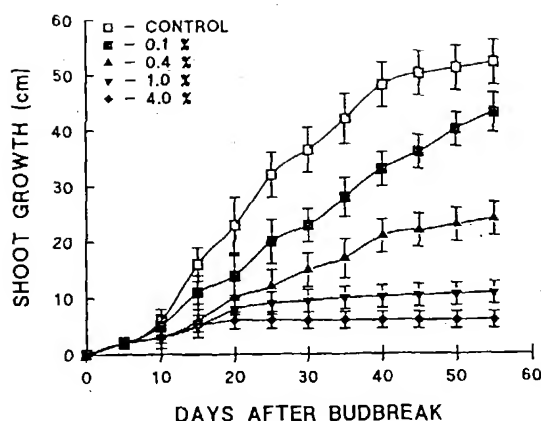


FIGURE 1. Shoot growth of potted 1-year-old 'Delicious' apple trees treated with 0, 0.1, 0.4, 1.0, and 4.0% paclobutrazol in Surfactant WK. Tree trunks were hand painted to a length three times the diameter of the trunk 10 cm above the soil line. Bars indicated  $\pm$  SEM.

## 2. Experiment 2

'Delicious' trees on seedling rootstock similar to those described above were treated as in experiment 1, with the following modifications. Tree trunks were hand painted with a 5.0% triazole solution to a standard length of 10 cm. In addition to paclobutrazol, two additional triazoles, each at 5.0% — (2RS,3RS)-1-(4-chlorophenyl)-4,4-dimethyl-1-2-(1,2,4-triazol-1-yl)-penten-3-ol (triapenthenol, Mobay Chemical Corp.) and BAS111 (BASF Corp.) — were applied in each of four solvent mixtures: Surfactant WK, Surfactant WK:isopropanol (1:1, v:v), propylene glycol, and propylene glycol:isopropanol (1:1, v:v). Again, the strongest shoot closest to the heading cut was retained and measured weekly for 11 weeks. There were six trees per replication in a completely randomized design.

## B. FIELD TRIALS

On July 14, 1988, ten actively growing apple, cherry, or apricot trees budded in August 1987 were selected in a commercial nursery for trunk paint trials. A 2.5% solution of uniconazole (E)-(1-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-ol- (Valent Chemical Corp.) was applied with a small brush to a 15-cm section of trunk approximately 10 cm above the soil line. The adjuvants used were: isopropanol, Regulaid® (Kalo Agricultural Chemicals, Inc.), Tween-20, X-77, Surfactant WK, propylene glycol, dipropylene glycol, Herbi-Max® (Loveland Industries, Inc.), and diesel:toluene (1:1, v:v). Solutions were applied sparingly to avoid drips down the trunk into the soil. Tree height was measured just prior to digging on August 2 and 26, and again on October 27, 1988.

# III. RESULTS AND DISCUSSION

## A. GREENHOUSE TRIALS

### 1. Experiment 1

Trunk bark applications of paclobutrazol in Surfactant WK showed a response to dosage in the range of 0.1 to 4.0% (Figure 1). At 0.1%, growth was temporarily suppressed, but then resumed at a rate similar to that of controls. There was a small amount of cuticle peeling on the painted area of the trunk. This peeling did not affect vigor, as growth was not slowed by the adjuvant mixture alone. In subsequent trials when adjuvant alone was applied to young trees with actively growing shoots, growth was slowed temporarily.<sup>12</sup>



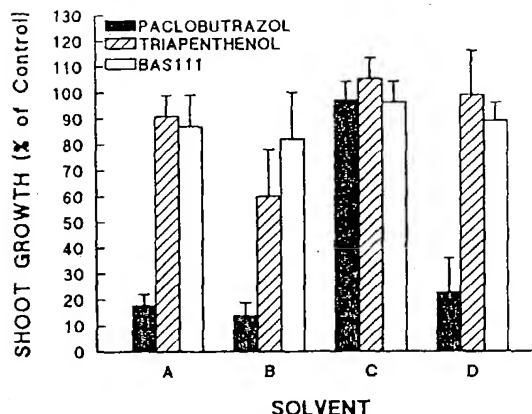


FIGURE 2. Shoot growth (expressed as percent of control) of potted 1-year-old 'Delicious' apple trees treated by painting a 10-cm length of trunk 10 cm above the soil line. Paclobutrazol, triapenthenol, or BAS111 were applied as a 5.0% solution in (A) Surfactant WK, (B) Surfactant WK:isopropanol (1:1), and (C) propylene glycol. Bars indicate  $\pm$  SEM.

## 2. Experiment 2

Three triazoles with varying degrees of persistence were applied to 1-year-old apple trunks in one of four adjuvant mixtures. Using Surfactant WK as the carrier, the shoot growth of treated trees after 11 weeks was in the order: paclobutrazol > triapenthenol > BAS111 (Figure 2). Whether this is due to a difference in uptake or metabolism within the tissue is uncertain, although other reports have shown that the metabolism of BAS111 is more rapid in apple tissue than is paclobutrazol or triapenthenol.<sup>12</sup> The addition of isopropanol to Surfactant WK improved the degree of growth reduction with both triapenthenol and BAS111. Propylene glycol did not have the penetrating properties, as did Surfactant WK. The addition of isopropanol, however, significantly improved its performance (Figure 2). When isopropanol, methanol, or ethanol alone was used in the past, drying occurred too quickly, resulting in little or no growth control.<sup>1</sup>

## B. FIELD TRIALS

Uniconazole is a GBI very similar to paclobutrazol in structure but may have a greater physiological effect.<sup>15</sup> In most of the adjuvants listed above, 2.5% uniconazole dissolved quite readily. However, even with mild heating, all the chemical did not enter the mixture of diesel:toluene. In spite of this, the treatment was applied, and the trees evaluated for phytotoxicity in September. The nine adjuvants were selected mainly for their availability. Of the nine adjuvants, those containing light paraffins such as Herbimax crop oil and diesel:toluene were the most injurious. About 40% of the trees treated with diesel:toluene died within 30 d. Trees treated with X-77 showed symptoms similar to those treated with Herbimax, including blistering and cuticle peeling (data not shown).

Most treatments resulted in growth suppression within 20 d (Figure 3). On apple, the adjuvant showing the greatest growth suppression and the least cuticle damage was Surfactant WK. Dipropylene glycol had effects similar to Surfactant WK. On cherry trees, the strongest effect again was achieved with Surfactant WK, followed by propylene glycol (Figure 3). Apricot trees showed the strongest response with X-77; however, there was considerable bark blistering and peeling. Of the other adjuvants tested, Surfactant WK gave the longest control. With some of the treatments, apricot was the only species to show considerable regrowth at the end of the growing season (Figure 3).

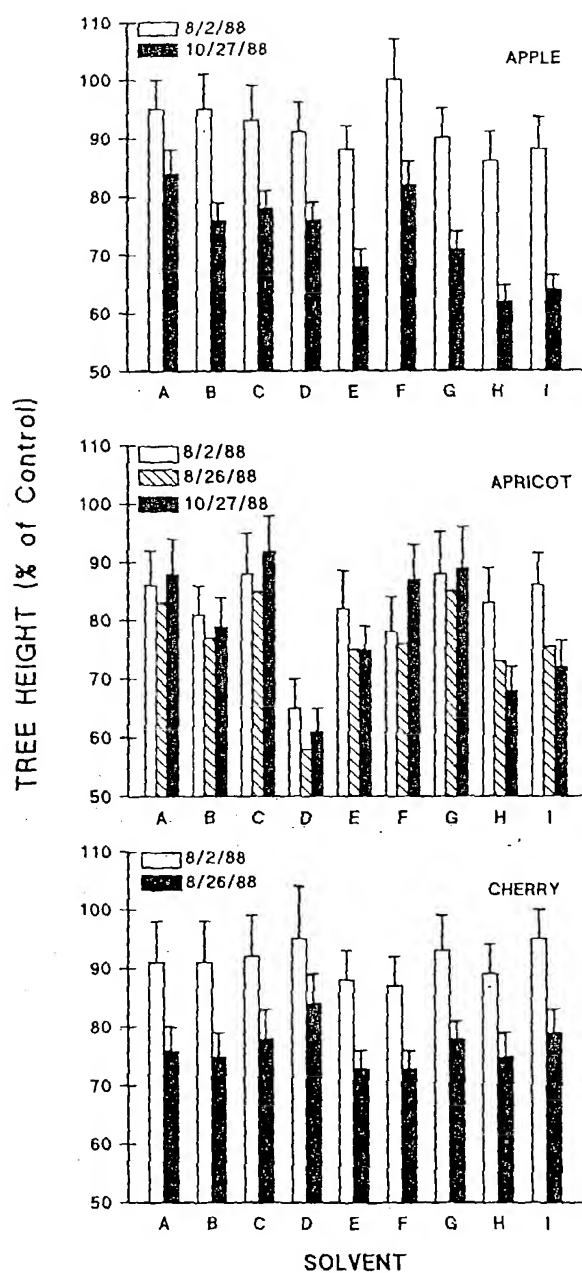


FIGURE 3. Shoot growth (expressed as percent of control) of field-grown 1-year old apple, apricot, and cherry trees treated July 14, 1988 and measured August 2 and 26 and October 27, 1988. Uniconazole was applied by painting a 15-cm length of trunk 15 cm above the soil line with a 2.5% solution of (A) isopropanol, (B) Regulaid, (C) Tween 20, (D) X-77, (E) Surfactant WK, (F) propylene glycol, (G) dipropylene glycol, (H) Herbi-Max, and (I) diesel:toluene (1:1). Bars indicated  $\pm$  SEM.

#### IV. CONCLUSIONS

The results from both greenhouse and field trials support the feasibility of the trunk bark method of application. The mixture of propylene glycol:isopropanol (1:1) appears to work well on trees in the greenhouse for certain triazoles. The addition of isopropanol to either triapenthenol or BAS111 did not significantly increase efficacy. Given its low toxicity, its relative effectiveness with certain compounds, and its low phytotoxicity, this adjuvant mixture appeared to be suitable for further trials. The triazole GBIs used in these trials appear to have inherently low phytotoxicity. However, perhaps less persistent triazoles would be more suitable for this type of treatment, to minimize environmental contamination.<sup>3</sup>

With young nursery trees, it is conceivable that trees of any height may be achieved by the correct timing and dosage. Preliminary trials with a spray wand indicate that the trunk bark treatment may be mechanized quite easily. Other reports have shown trunk paint applications to be effective on ornamental species and mature, bearing fruit trees using Surfactant WK as carrier.<sup>2,13</sup> Preliminary trials on mature fruit trees (data not shown) indicated that propylene glycol:isopropanol (1:1, v:v) was not effective. This may be due to the more rapid drying time, compared with Surfactant WK, under field conditions. In this trial, the best and least injurious response on nursery-grown trees was obtained with Surfactant WK, dipropylene glycol, and propylene glycol.

There may be other compounds that are amenable to this method of application for growth control. Preliminary trials suggest that low rates of glyphosate applied in an aqueous solution to the lower bark of young peach and apple trees may control growth without phytotoxicity (data not shown). In the past, foliar applications of glyphosate have been either phytotoxic or have resulted in temporary cessation of growth followed by regrowth of multiple short shoots just below the shoot tip.<sup>6</sup>

In the future, the successful treatment will be one which is inexpensive, nontoxic, controls growth for a known period of time so that treatments may be reapplied if needed, and has low environmental persistence.

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## Chapter 54

RELATIONSHIP OF CHEMICAL CLASSIFICATION AND  
HYDROPHILIC-LIOPHILIC BALANCE OF SURFACTANTS TO  
UPPER LEAF-SURFACE PENETRATION OF GROWTH  
REGULATORS IN APPLES

Siyuan Tan and Garvin D. Crabtree

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## ABSTRACT

The effect of surfactants on the movement of  $^{14}\text{C}$ -labeled plant growth regulators through the stomatal upper surface of apple (*Malus pumila* M. 'Golden Delicious') leaf discs was studied by presoaking the discs in 1% solutions of nonionic surfactants. Penetration was measured by detecting changes in the radioactivity of the solution in glass cylinders sealed to the upper surface of the discs. Penetration of 2,4-D[(2,4-dichlorophenoxy)acetic acid] and  $\beta$ -NAA (2-naphthaleneacetic acid) was significantly increased by Pegosperse® 200-ML; no significant effect was observed from Ethox HCO-16, Hyonic® NP 40, Pegeste® SML, and Span® 20, which had the same hydrophilic-lipophilic balance ( $\text{HLB} = 8.6 \pm 0.5$ ) as Pegosperse 200-ML. Penetration of 2,4-D and  $\beta$ -NAA decreased linearly as surfactant HLB increased from 3.5 (Pegosperse 100-O) to 14.6 (Pegosperse 600-ML). Penetration of maleic hydrazide (MH) (1,2-dihydro-3,6-pyridazinedione) was not affected by any surfactant tested.

## I. INTRODUCTION

Surfactants reduce the surface tension of a pesticide solution and can improve coverage and foliar absorption of the pesticide.<sup>2,3,8</sup> However, this is not the only role of surfactants in foliar absorption. In their studies on apples, Westwood and Batjer<sup>9</sup> observed successive increase in NAA absorption by increasing the concentration of surfactant far beyond that required for minimum surface tension. Lownds et al.<sup>5,6</sup> also found a similar phenomenon in cowpea (*Vigna unguiculata* L., Walp.) and reported that the effects depended on the type of surfactant used. They attributed this to the changes in interface area, drying time, and stomatal penetration caused by surfactants and considered that this also could be due to interactions between surfactant, NAA, and the plant surface. Kirkwood et al.<sup>4</sup> reported that the penetration of MCPA and MCPB through isolated abaxial cuticles of broad beans (*Vicia faba* L.) was associated with surfactant HLB. Since the mechanism by which surfactants facilitate foliar entry and movement of pesticides has received little attention,<sup>3</sup> the specific interactions between plant, solute, and surfactant are still not explained.<sup>6,7</sup> The objective of this experiment was to investigate the relationships of chemical classification and HLB of surfactants to their effects on the foliar absorption of plant growth regulators. The responses to be studied were not to include effects from changing surface tension, drying time, and stomatal entry of the spray solution.

## II. MATERIALS AND METHODS

Fully expanded apple leaves were sampled in October 1988 from 5-year-old Golden Delicious trees on MM106 root stocks. Leaf discs were prepared with a 17.5-mm cork borer, avoiding midribs and large veins. The discs were washed with distilled water and placed in beakers containing 1% (v/v) solutions of different nonionic surfactants. Each surfactant treatment had five discs in a beaker. The surfactants with their chemical classification and HLB are shown in Table 1. Additional information on the characteristics of these products can be found in *McCutcheon's Emulsifiers & Detergents*.<sup>1</sup> The discs were soaked in the surfactant solutions for 48 h in the dark at 25°C and then washed with tap and distilled water.

Glass cylinders with a height of 15 mm and an internal diameter of 12.3 mm were touched to Permabond 910® adhesive (Permabond International Division, Englewood, NJ) and then positioned on the upper surface of the leaf discs. The discs and glass cylinders were placed in 9 × 2-cm petri dishes lined with pieces of moistened filter papers. After about 45 min, when the adhesive had dried, 0.5 ml of  $^{14}\text{C}$ -labeled plant growth regulator

TABLE 1  
Chemical Classification, HLB, and Manufacturers of Surfactants Tested

Surfactant trade name	Chemical classification	HLB	Manufacturer	
			Name	Address
Ethox HCO-16	Ethoxylated triglycerides	8.6	Ethox Chemicals, Inc.	P.O. Box 5094 Sta. B Greenville, SC 29606
Hyonic NP 40	Alkyl phenoxy polyoxyethylene ethanol	8.6	Henkel Corp.	350 Mt. Kemble Ave. Morristown, NJ 07960
Pegeste SML	Sorbitan esters	8.6	GAF Chemicals Corp.	1361 Alps Rd. Wayne, NJ 07470
Pegosperse 100-O	Diethylene glycol monooleate	3.5	Lonza Inc.	17-17 Route 208 Fair Lawn, NJ 07410
Pegosperse 200-ML	Polyethylene glycol 200 monolaurate	8.6	Lonza Inc.	17-17 Route 208 Fair Lawn, NJ 07410
Pegosperse 600-ML	Polyethylene glycol 600 monolaurate	14.6	Lonza Inc.	17-17 Route 208 Fair Lawn, NJ 07410
Span 20	Sorbitan monolaurate	8.6	ICI Americas Inc.	Concord Pike and New Murphy Rd. Wilmington, DE 19897

solution, buffered by 40 mM citric phosphate (pH 3.0) and containing 0.1 mM sodium azide, was pipetted into each glass cylinder. The concentrations of 2,4-D,  $\beta$ -NAA, and MH were 0.78, 0.54, and 8.92 mM, respectively. The specific activities of 2- $^{14}$ C-labeled 2,4-D, carboxy- $^{14}$ C-labeled  $\beta$ -NAA and 4,5- $^{14}$ C-labeled MH were 28.0, 6.6, and 10.2 mCi/mmol, respectively. The petri dishes were covered and placed in the dark in a 25°C water bath. The atmosphere and filter papers inside the petri dish were kept saturated with distilled water.

After 24 h, the solution of  $^{14}$ C-labeled growth regulators in each glass cylinder was carefully collected into a liquid scintillation counting vial. Each leaf disc with attached glass cylinder was washed with 7 ml of AquaMix cocktail (ICN Biomedicals, Inc., Costa Mesa, CA) and the washing solution was added to the vial. Radioactivity of the collected solutions was measured by a liquid scintillation counter (Beckman, Model LS 7000). Samples containing 0.5-ml solutions of the initial  $^{14}$ C-labeled and normal, nonradioactive growth regulators were also prepared to determine the original radioactivity present in the solution and background, respectively. The amount of  $^{14}$ C-labeled growth regulator penetrating the leaf surface was determined by subtracting the quantity of  $^{14}$ C-label in the collected solution from the amount originally present.

Trials were conducted with 2,4-D,  $\beta$ -NAA, and MH under the same conditions using completely randomized designs with four replications. Data were subjected to variance analysis. The means of the surfactant chemical classification were separated by Newman-Keuls tests and the effect of HLB on the penetration of the growth regulators was evaluated by regression analysis.

### III. RESULTS AND DISCUSSION

Penetration of 2,4-D and  $\beta$ -NAA through the stomatal upper surface of apple leaf discs was significantly increased by previously soaking the leaf discs in 1% Pegosperse 200-ML solution (Table 2). This treatment doubled and tripled the penetration of 2,4-D and  $\beta$ -NAA, respectively, compared with the water control. Surfactants from other chemical groups, but

TABLE 2  
Relationship of Chemical Classification of Nonionic Surfactants to the Penetration of  
<sup>14</sup>C-Labeled 2,4-D and  $\beta$ -NAA Through the Astomatal Upper Surface  
of Apple Leaf Discs

Surfactants	2,4-D		$\beta$ -NAA	
	Absorbed by leaf discs (cpm) <sup>a</sup>	Absorption <sup>b</sup> (%)	Absorbed by leaf discs (cpm) <sup>a</sup>	Absorption <sup>b</sup> (%)
Water control	1800 a <sup>c</sup>	33	780 a	9
Ethox HCO-16	2500 a	45	620 a	7
Hyonic NP 40	2800 a	51	1600 ab	18
Pegeste SML	2700 a	49	860 a	10
Pegosperse 200-ML	4100 b	74	2340 b	26
Span 20	3000 a	55	540 a	6

<sup>a</sup> Counts per minute (cpm) absorbed by leaf discs = (cpm added in the glass cylinder originally) - (cpm left in the cylinder).

<sup>b</sup> Absorption percentage = (cpm absorbed by leaf discs)/(cpm added in the cylinder originally)  $\times$  100.

<sup>c</sup> Means within columns followed by the same letter are not significantly different 15% Newman-Kuels test.

which had the same HLB as Pegosperse 200-ML, slightly changed the amount of 2,4-D and  $\beta$ -NAA penetration, but the effects were not significant. Chemical classification of the surfactants appears to be an important factor affecting penetration of the plant growth regulators. MH penetration was not affected by any surfactant tested under the conditions of this experiment. The finding that Pegosperse 200-ML increased the penetration of water-insoluble 2,4-D and  $\beta$ -NAA, but did not affect the penetration of water-soluble MH, indicates that the effect of surfactants on penetration is also related to growth regulator type.

Three Pegosperse surfactants varying in HLB were used in investigating the relationship between this factor and growth regulator penetration. The three surfactants, Pegosperse 100-O, 200-ML, and 600-ML, had HLBs of 3.5, 8.6, and 14.6 respectively. Penetration of 2,4-D and  $\beta$ -NAA decreased linearly as the HLB of Pegosperse surfactants increased from 3.5 to 14.6 (Figure 1). Although the three Pegosperse materials belong in the same chemical group, Pegosperse 600-ML did not significantly increase the penetration of 2,4-D, compared with the water control. It appears that both HLB and chemical classification of surfactants affect the penetration of 2,4-D and  $\beta$ -NAA. As had also been found for the chemical classes, penetration of MH was not influenced by the HLB of Pegosperse surfactants.

In this experiment, since the growth regulator solution had the same interface area for all surfactant treatments and the upper surface of apple leaves had no stomata, the possible effects of surfactants on wetting and stomatal entry of the solution could be excluded. Possible chemical reaction of surfactants and growth regulators before the penetration could also be excluded since surfactants were not added in the growth regulator solutions. The results show that nonionic surfactants could have effects on foliar penetration of plant growth regulators in addition to changing wetting, drying time, and stomatal entry of the spray solution. The effects are related to the chemical classification and HLB of the surfactants and depend on the type of growth regulators.

### ACKNOWLEDGMENTS

We thank Rhone-Poulenc AG Company and Uniroyal Chemical Company, Inc. for the  $\beta$ -NAA and MH, and the chemical companies listed in Table 1 for the surfactants used in this study.

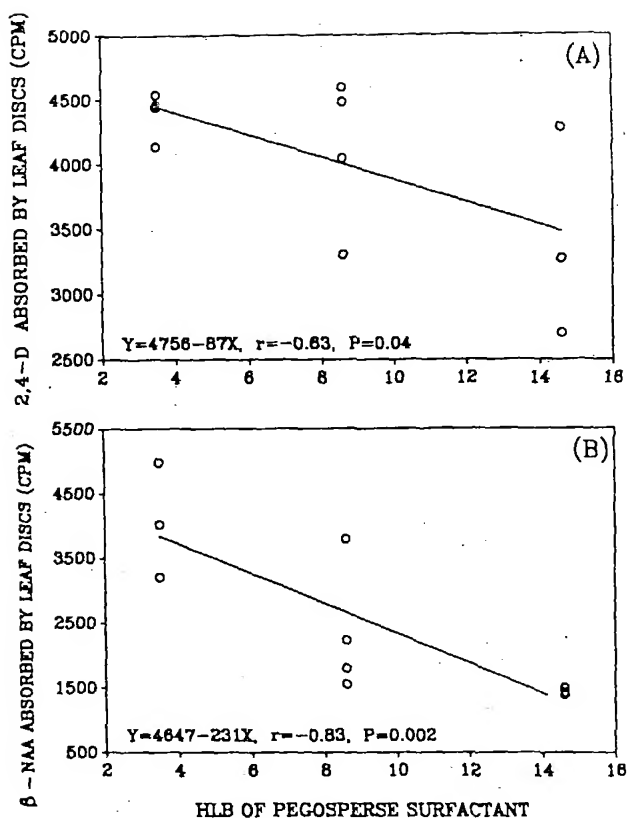


FIGURE 1. Relationship between the HLB of Pegosperse surfactants and penetration of 2,4-D (A) and  $\beta$ -NAA (B) through the astomatal upper surface of apple leaf discs.

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## Chapter 55

POSSIBLE METHODS TO INCREASE EFFICACY OF  
GIBBERELIC ACID APPLIED TO NAVEL ORANGE TREES

Charles W. Coggins, Jr., Gilbert L. Henning,\* and Michael F. Anthony

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\* Sadly, Mr. Henning passed away before the publication of this book. We salute his contributions to the field of Botany and Plant Sciences.

## ABSTRACT

Reports from Israel and South Africa indicate the effectiveness of preharvest applications of gibberellic acid ( $GA_3$ ) to citrus can be improved substantially by lowering the pH of the treatment solution or by the addition of surfactant. Silwet® L-77 (Union Carbide) — a polyalkylene oxide modified dimethylpolysiloxane — has been reported to be especially effective. Since increased  $GA_3$  efficacy on citrus is of both scientific and economic interest, we conducted a field experiment at two California locations (Riverside and Tulare Counties) to assess the impact of pH (~4.2 vs. ~7.8), L-77 (0.025% v/v), and combinations thereof on the biological effectiveness of preharvest applications of  $GA_3$  (2.5, 5, and 10 ppm) in delaying *Citrus sinensis* (L.) Osbeck rind senescence. Treatments were applied in October (8 trees/treatment/location) at the rate of ~8000 l/ha and fruit were evaluated 14 to 29 weeks later. Based on rind-color and rind firmness data, we observed the following trends: (1) low pH, by itself, did not lead to a significant increase in efficacy for any  $GA_3$  rate, and (2) presence of L-77 increased  $GA_3$  efficacy regardless of pH level. Clearly, of the two factors evaluated, inclusion of L-77 in the spray solution appeared most promising.

## I. INTRODUCTION

Gibberellic acid ( $GA_3$ ) is registered with the United States Environmental Protection Agency for preharvest use to delay certain aspects of fruit senescence on grapefruit (*Citrus paradisi* Macf.) in Florida and Texas and on navel and 'Valencia' orange (*Citrus sinensis* L., Osbeck), lemon (*Citrus limon* L., Burm.f.) and 'Minneola' tangelo (*Citrus paradisi* × *Citrus reticulata* Blanco) in California.<sup>3</sup> Most of the  $GA_3$  used on citrus in the United States is applied to navel orange groves in California where a high percentage of groves receive dosages in the range of 25 to 100 g a.i./ha.<sup>1</sup>  $GA_3$  is used for similar purposes in other citrus producing countries.

In the United States, the retail price of formulated  $GA_3$  is approximately \$1.50/g a.i., and there is considerable interest in techniques that would provide the desired response at a lower dosage. Gilfillan<sup>4</sup> of South Africa found that when the  $GA_3$  spray was acidified to pH 4.0 with sulfuric acid, the spray concentration could be reduced to approximately 70% of the concentration used without acidification. Considerable enhancement of  $GA_3$  activity when applied in low pH solutions in Israel has been reported by Greenberg et al.,<sup>6</sup> and by Greenberg and Goldschmidt.<sup>5</sup> Greenberg and Goldschmidt reported that the type of acidifying agent used does not appear to be critical. There seems to be general agreement that improved effectiveness of  $GA_3$  at low pH is due to improved uptake of the undissociated molecule, in comparison to the dissociated form, which would prevail at higher pH values.

Surfactants are commonly added to the  $GA_3$  sprays applied to California citrus groves. However, we have no recommendation as to which surfactant to use. Greenberg et al.<sup>6,7</sup> have reported better uptake and physiological response of  $GA_3$  when Silwet L-77 was used than when Triton® B-1956 surfactant was used on grapefruit in Israel. Silwet L-77 (Union Carbide, Danbury, CT) is a polyalkylene oxide modified dimethylpolysiloxane. Triton B-1956 (Rohm and Haas, Philadelphia, PA) is a formulation of a 77% modified phthalic glycerol alkyd resin plus 23% non-surfactant constituents. The Rohm and Haas product is widely used in  $GA_3$  spray preparations in California whereas the Union Carbide product is not.

The objective of the study reported here was to determine the relative influences of pH and surfactant on the efficacy of  $GA_3$  applied preharvest to navel orange trees in California.

## II. MATERIALS AND METHODS

Research was conducted at two experimental sites during the 1987 to 1988 crop year using a factorial design with eight blocks at each site. One tree per block was assigned to each  $3 \times 2 \times 2$  treatment combination. Each block also contained an untreated control tree. Factors consisted of three concentrations of  $GA_3$  (2.5, 5, and 10 ppm), absence and presence of L-77 (0.025%, v/v), and absence and presence of phosphoric acid.  $GA_3$  dosages were selected with the expectation of incremental increases in magnitude of response with each increase in concentration. Phosphoric acid was used because it is relatively nonphytotoxic when it is used at rates which achieve pH levels of 4.0 and higher (T. W. Embleton, personal communication) and because Greenberg and Goldschmidt<sup>5</sup> have reported that the type of acidifying agent is not critical. L-77 was used because Greenberg et al.<sup>6,7</sup> found better results with it than with B-1956. The concentration selected for L-77 was based on the report that  $GA_3$  uptake was optimum in the 0.025% range,<sup>7</sup> and on confirming biological testing we did on citrus fruits.<sup>8</sup>

The Porterville (Tulare County, San Joaquin Valley) site was in a grove of 22 year-old Frost nucellar 'Washington' navel orange trees on Troyer citrange (*Poncirus trifoliata* L., Raf  $\times$  *Citrus sinensis*) rootstocks. The Corona (Riverside County, southern California) site was in a grove of 22 year-old, old-line 'Washington' navel orange trees on Troyer citrange rootstocks. In summary, there were thirteen treatments, eight blocks of thirteen single-tree plots, and two experimental sites.

Treatments were applied with a handgun at approximately 30 kg/cm<sup>2</sup> at the rate of approximately 8,000 l/ha. Sprays were applied October 15, 1987 at the Porterville site and October 21, 1987 at the Corona site when fruit were dark green in color. Color-break on nontreated trees occurred approximately two weeks after treatments were applied.

Rind firmness and rind color were evaluated at 14, 24, and 29 weeks and 14 and 22 weeks after treatment at the Porterville and Corona sites, respectively. Rind firmness was determined by resistance to a 1.0-mm diameter puncture tip, described by Coggins and Lewis.<sup>2</sup> Puncture resistance was measured on 16 fruit/tree (2 punctures/fruit) for the 14-week samples. For subsequent evaluations, rind firmness was measured on 8 fruit/tree (4 punctures/fruit). Rind color was subjectively evaluated according to a 1 to 10 scale, where 1 = green, 5 = yellow, and 10 = reddish orange. Sixteen fruit/tree were evaluated for the 14-week samples and eight fruit/tree were evaluated subsequently.

## III. RESULTS AND DISCUSSION

### A. RIND COLOR

Delayed loss of chlorophyll and reduced rates of accumulation of carotenoid pigments are reliably obtained when  $GA_3$  treatments are made to navel orange trees when the fruits are green but approaching color-break. Rind color was thus used in this study as one of the assessments of the  $GA_3$  response. Rind color data appear in Table 1. Lower values depict fruit that are greener or less intensely orange, and thus lower values indicate a stronger  $GA_3$  response.

Analyses of variance followed by Duncan's multiple range tests (not shown) indicated clear rind color differences between the untreated control and 2.5 ppm  $GA_3$ . This difference existed regardless of the presence and/or absence of L-77 or phosphoric acid. Data in Table 1 show main effects. Significant differences in color were related to  $GA_3$  concentrations. In each of the evaluations, there were significant linear and quadratic components in the relationship between the magnitude of the color response and the log of the  $GA_3$  concentration. As anticipated, incremental increases in  $GA_3$  dosage gave measurable differences

TABLE 1  
Effects of L-77 Surfactant and pH on the Biological  
Effectiveness of Gibberellic Acid ( $GA_3$ ) Applied to  
'Washington' Navel Orange Trees as Measured by Delayed  
Coloring of the Rind<sup>a</sup>

	Rind color <sup>b</sup>				
	Porterville			Corona	
	Jan. 21	March 30	May 4	Jan. 29	March 23
$GA_3$ treatment <sup>c</sup> (ppm)					
2.5	6.02	7.72	8.69	6.77	7.66
5.0	5.43	7.14	8.37	6.46	7.24
10.0	4.88	6.70	7.87	5.75	6.63
Significance <sup>d</sup> (sig.)					
F	0.0001	0.0001	0.0001	0.0001	0.0001
Linear	0.0001	0.0001	0.0473	0.0025	0.0016
Quadratic	0.0001	0.0001	0.0001	0.0001	0.0001
L-77 <sup>e</sup>					
-	5.68	7.38	8.46	6.67	7.49
+	5.22	6.99	8.16	5.99	6.87
Sig. of F	0.0001	0.0004	0.0224	0.0001	0.0001
Acid <sup>f</sup>					
-	5.38	7.11	8.24	6.34	7.20
+	5.51	7.27	8.38	6.32	7.16
Sig. of F	NS	NS	NS	NS	NS
Untreated control	8.00	9.32	9.42	8.54	8.98

<sup>a</sup> Both experiments consisted of a factorial design with eight blocks of trees. One tree/block was assigned to each  $3 \times 2 \times 2$  treatment combination. Each block also contained an untreated control tree. Sprays were applied Oct. 15, 1987 at the Porterville site and Oct. 21, 1987 at the Corona site.

<sup>b</sup> Subjectively evaluated according to a 1 to 10 scale where 1 = green, 5 = yellow, 10 = reddish orange. Sixteen fruit/tree were evaluated in January and eight fruit/tree were evaluated subsequently.

<sup>c</sup> Main effects (across - and + L-77 and across - and + acid treatments).

<sup>d</sup> NS indicates lack of significance at 5% level. For all other situations, calculated probability values are shown. Linear and quadratic functions refer to log of  $GA_3$  concentrations.

<sup>e</sup> Main effects (across  $GA_3$  concentrations and across - and + acid treatments). Plus indicates L-77 was included at a concentration of 0.025% v/v.

<sup>f</sup> Main effects (across  $GA_3$  concentrations and across - and + L-77 treatments). Plus indicates phosphoric acid ( $H_3PO_4$ ) was added. Resulting pH values covered the range of 4.1 to 4.4. The pH of sprays containing no phosphoric acid ranged from 7.7 to 8.0.

in rind color. Therefore, it is clear that our experimental conditions were sufficiently sensitive to measure differences in  $GA_3$ -dosage responses and thus sufficiently sensitive to detect appreciable changes in  $GA_3$  effectiveness caused by low pH and by absence or presence of the L-77 surfactant.

Based on the pH and surfactant main effects shown in Table 1, we have concluded that low pH did not provide a significant increase in the effectiveness of  $GA_3$ , but that L-77 did. Probability values presented in Table 1 strongly support this conclusion.

TABLE 2  
Effects of L-77 Surfactant and pH on the Biological Effectiveness of  
Gibberellic Acid ( $GA_3$ ) Applied to 'Washington' Navel Orange Trees as  
Measured by Delayed Softening of the Rind<sup>a</sup>

	Rind firmness <sup>b</sup>				
	Porterville			Corona	
	Jan. 21	March 30	May 4	Jan. 29	March 23
$GA_3$ treatment <sup>c</sup> (ppm)					
2.5	298	252	240	387	346
5.0	306	268	252	405	351
10.0	318	280	262	433	372
Significance <sup>d</sup>					
F	0.0001	0.0001	0.0001	0.0001	0.0001
Linear	0.0194	0.0001	0.0002	0.0038	NS
Quadratic	0.0001	0.0001	0.0001	0.0001	0.0001
L-77 <sup>e</sup>					
-	303	265	246	392	343
+	311	269	257	424	369
Sig. of F	0.0031	NS	0.0001	0.0001	0.0001
Acid <sup>f</sup>					
-	306	266	253	405	356
+	308	268	250	411	356
Sig. of F	NS	NS	NS	NS	NS
Untreated control	265	230	210	330	304

<sup>a</sup> Both experiments consisted of a factorial design with eight blocks of trees. One tree/block was assigned to each  $3 \times 2 \times 2$  treatment combination. Each block also contained an untreated control tree. Sprays were applied Oct. 15, 1987 at the Porterville site and Oct. 21, 1987 at the Corona site.

<sup>b</sup> Grams resistance to a 1.0 mm diameter puncture tip. Sixteen fruit/tree and 2 punctures/fruit in January. Eight fruit/tree and 4 punctures/fruit subsequently.

<sup>c</sup> Main effects (across - and + L-77 and across - and + acid treatments).

<sup>d</sup> NS indicates lack of significance at 5% level. For all other situations, calculated probability values are shown. Linear and quadratic functions refer to log of  $GA_3$  concentrations.

<sup>e</sup> Main effects (across  $GA_3$  concentrations and across - and + acid treatments). Plus indicates L-77 was included at a concentration of 0.025% v/v.

<sup>f</sup> Main effects (across  $GA_3$  concentrations and across - and + L-77 treatments). Plus indicates phosphoric acid ( $H_3PO_4$ ) was added. Resulting pH values covered the range of 4.1 to 4.4. The pH of sprays containing no phosphoric acid ranged from 7.7 to 8.0.

## B. RIND FIRMNESS

It is widely acknowledged that  $GA_3$  delays softening of citrus rind tissue and that delayed softening is closely associated with delayed senescence and various benefits to be derived therefrom. Therefore, rind firmness was used to help determine the relative influence of pH and surfactant on  $GA_3$  effectiveness. Rind firmness data appear in Table 2. Higher values depict fruit with firmer and less senescent rinds. Higher values indicate a stronger  $GA_3$  response.

The results presented in Table 2 and the results of Duncan's multiple range tests regarding all 13 treatments (not shown) lead to essentially the same conclusions with respect to  $GA_3$  concentration and main effects of pH and surfactant already presented for the rind color responses. Therefore, the details will not be repeated in the text.

In a third statistical evaluation of the data (*t* tests not presented), we saw evidence of a modest improvement of rind firmness in the effectiveness of  $GA_3$  from low pH when  $GA_3$



was applied at 2.5 ppm in the presence of L-77. We saw no measurable increase in GA<sub>3</sub> response from low pH in any other situation included in our study. Since main effects were strong for surfactant and essentially absent for pH, we have concluded that the potential for increasing the effectiveness of preharvest applications of GA<sub>3</sub> in California navel orange groves is considerably higher with surfactants than from the control of pH of the spray mixture, and our further attempts to increase efficacy should concentrate on surfactants. Why substantial benefits from low pH were obtained in Israel and South Africa and not in our study is an unresolved question.

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## Chapter 56

**DAMINOZIDE INDUCED EFFECTS ON *VICIA FABA* L. AND THE  
IMPORTANCE OF SPRAY ADJUVANTS**

Christopher F. Green

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## ABSTRACT

In three field experiments, the influence of daminozide as Alar® (Uniroyal Inc.) or Dazide® (Fine Agrochemicals Ltd.) on both winter- and spring-sown *Vicia faba* L. was assessed. Full-dose-rate response curves were constructed using up to 3.2 kg ha<sup>-1</sup> of daminozide and comparing a range of adjuvants including alkyl phenol ethylene oxide condensate (Agral®, ICI); ethoxylated tallow amine (Hyspray®, Fine Agrochemicals Ltd); acidified soyal lecithin (LI700, Loveland Industries Inc.), and emulsified mineral oil (Actipron®, Bayer Co.).

Daminozide altered the partition of plant phytomass in favor of pods at the expense of the lower stem. Emaciation of this stem increased the propensity of the stand to brackling (lodging). The influence of daminozide on *V. faba* could thus be assessed by calculating the fraction of phytomass present as pods ( $p_p$ ) and by measuring the degree of brackling ( $\ell$ ).

Relating both  $p_p$  and  $\ell$  to the rate of daminozide applied suggested that the rate of response was strongly dependent on adjuvant chemistry. Efficiency of response was maximized by adding LI700 to the spray solution, followed by Actipron, Hyspray, and Agral. Increasing  $p_p$  promoted seed yield when  $\ell$  was not increased over a threshold value.

## I. INTRODUCTION

The potential use of synthetic plant growth regulators in crops of *V. faba* has been discussed by Keller and Bellucci.<sup>20</sup> Daminozide (*N*-dimethyl aminosuccinamic acid) inhibits auxin synthesis<sup>25</sup> and influences flowering physiology in some species (e.g., *Solanum melongena*<sup>10</sup> and *Cyamopsis tetragonoloba*<sup>38</sup>). For *Malus pumila*, daminozide increased the rate of fruit production proportional to increases in flowering.<sup>3,37</sup> These responses may be due to daminozide-induced changes in the activity of endogenous auxin, gibberellins, and cytokinins.<sup>19</sup>

For *Carya illinoensis*, foliar daminozide affected biomass fractionation by increasing nut production from a stimulation of staminate and pistillate bud development.<sup>22</sup> Daminozide exerts pronounced manipulation of growth and development for podded crops. Increased assimilation by *Glycine max*,<sup>39</sup> more branches, flowers, pods and seeds of *Phaseolus mungo*,<sup>1</sup> and higher seed yield, protein content, and carbohydrate production of *C. tetragonoloba* all followed treatment with daminozide.<sup>38</sup>

Applications of daminozide to spring-sown *V. faba* crops at the four-true-leaf stage increased seed yield by promoting branching and podding.<sup>9,23</sup> While McEwen<sup>23</sup> measured reduced mean seed mass, El-Beltagy, et al.<sup>9</sup> recorded increases in seed weight and the number of seeds per pod, classically the most stable yield component.<sup>7</sup>

Studies during 1986 and 1987 measured increases in seed yield of *V. faba* with daminozide applied at the onset of podding.<sup>11</sup> Responses measured by Stapleton<sup>29</sup> occurred at 5.3 kg of daminozide per hectare. This chapter presents research conducted during 1986, 1987, and 1988 on winter-sown crops of *V. faba* in the field. The studies explored the physiological nature by which *V. faba* responded to applied daminozide and the influence of spray adjuvants admixed to the spray solution, on the nature of the response curves. The role of adjuvants as one component of an integrated agronomic rationale and its physiological understanding is emphasized.

## II. MATERIALS AND METHODS

### A. SITES AND TREATMENTS

#### 1. Waltham-on-the-Wolds, 1986

Winter beans (cv. Banner) were sown at a rate of 18 seeds per square meter into a clay soil in November 1985. Weed control involved a postsowing application of 1.5 kg of simazine per hectare (Gesatop® 50 WP, Ciba Geigy). Chocolate spot was controlled with 1 kg of chlorothalonil per hectare (Bravo® 500, BASF) in May at the onset of flowering. Eighty-five percent daminozide (Alar®) was applied at the onset of podding (June 1986) in 300 l of water per hectare, at 2 bar, through 110° fan jet nozzles (Spraying Systems).

Treatments comprised seven rates of Alar (0, 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 kg ha<sup>-1</sup>) with either soyal lecithin acidified with propionic acid (LI700) at 0.5% (v/v) or a 90% alkyl phenol ethylene oxide condensate wetter (Agral) at 0.1% (v/v). Two replicate 1.5 × 5-m plots of each treatment were arranged in a randomized block design.

#### 2. Saxelby Park, 1987

At Saxelby Park, Leicestershire, U.K., *V. faba* (cv. Bourdon) was sown on November 2, 1986, at a seed rate of 21 seeds per square meter, into a medium clay loam. Weed control involved 1.15 kg of simazine per hectare on November 3, 1986, followed by 0.94 kg of alloxym-sodium per hectare (Clout®, Rhone-Poulenc) on April 8, 1987. *Botrytis* spp. were controlled using 500 g of vinclozolin per hectare (Ronilan®, BASF) with 250 g of carbendazim per hectare (Bavistin®, BASF) on May 2, 1987, followed by 1 kg of chlorothalonil per hectare on June 28, 1987, and again on July 27, 1987.

Daminozide (Alar) was applied at the onset of podding (June 18, 1987) in 200 l of water per hectare, at 1 bar, through low-pressure calibrated spray nozzles (Lurmark). Six rates of daminozide (0, 0.425, 0.85, 1.275, 1.7, and 2.55 kg ha<sup>-1</sup>) were applied with and without LI700 in the spray solution at a 0.5% dilution (1 l ha<sup>-1</sup>). Rates equivalent to 0, 0.5, 1.0, 1.5, 2.0, and 3.0 kg of Alar per hectare were tried. Treatments were arranged as a factorial combination utilizing three randomized blocks of 36 plots each measuring 2 m wide and 20 m long.

#### 3. Prestwold Hall, 1988

At Prestwold Hall, Leicestershire, U.K., *V. faba* (cv. Bourdon) was sown on November 2, 1987, at a rate of 28 seeds per square meter into a sandy loam. Simazine at 1.0 kg ha<sup>-1</sup> with 1.14 kg of carbetamide (Kerb®, pbi) were applied on December 7, 1987, and the only herbicides used. *Botrytis* spp. were prevented using 0.25 kg of carbendazim per hectare (Focal®, Schering) on April 22, 1988, followed by 500 g of chlorothalonil per hectare on May 13, 1988, and 334 g of iprodione per hectare with 334 g of thiophanate-methyl per hectare (Compass®, Rhone-Poulenc) on June 20, 1988. The fertilizer consisted of 114 kg of K<sub>2</sub>O per hectare as muriate of potash.

Daminozide (Dazide, 85%) was applied at 0, 0.5, 1.5, 2.5, and 4.0 kg ha<sup>-1</sup> either alone or with a tallow amine (1%, v/v; Hyspray), a 97% emulsified refined mineral oil (1%, v/v; Actipron) or acidified lecithin (0.5%, v/v; LI700). Foliar applications at 2 bar through 110° fan jet nozzles gave an output of 200 l ha<sup>-1</sup> at the onset of podding (June 8, 1987). Treatments were arranged in three randomized blocks of plots 2.5 m wide and 10 m long.

### B. RECORDS OF CROP PERFORMANCE

Samples from two 1-m<sup>2</sup> quadrats were taken from each plot to assess phytomass partitioning by dividing plants into seed husks, and vegetative tissue (above and below the uppermost podded node at Saxelby Park). Samples were dried for 72 ± 3 h at 85 ± 5°C



in a ventilated oven and weighed. Lodging area was assessed using the technique of Green and McDonald.<sup>15</sup> In 1986, yield alone was measured. In 1988, ten petri dishes were placed in the base of each plot and used to assess the mean level of spray solution transmitted through the canopy at spraying ( $\tau$ ).

Statistical analyses of all proportions were conducted following a logit transformation ( $0.5 \ln\{[P\% + 0.05]/[100.05 - P\%]\}$ ), avoiding problems arising from  $P\% = 0$  or  $100\%$ .<sup>40</sup>

### III. RESULTS

Field responses from daminozide-adjuvant combinations can rarely be assessed by measuring daminozide-induced effects on seed yield ( $\gamma_s$ ).  $\gamma_s$  is a function of several variables, each of which may be influenced by daminozide applications ( $\delta$ ) and some of which may prove to be correlated. In addition, daminozide may modify physiological yield determinates, with each variation causing additive or opposite effects on  $\gamma_s$ . My suggestion for a simplified dynamic partitioning model, relating variables and parameters deterministic of  $\gamma_s$  can be written as

$$\gamma_s = \rho_p \cdot \rho_s \cdot M_o \cdot \{1 - (\alpha \cdot \ell)\} \quad (1)$$

where, for an unlodged stand,  $\rho_p$  is the fraction of the total plant biomass divested into pods and  $\rho_s$  is the proportion of pod phytomass present as seed (thus,  $\rho_p \cdot \rho_s$  = harvest index).  $M_o$  is the total biomass as a potential for that crop, where lodging ( $\ell$ ) = 0, and  $\alpha$  is the fractional yield reduction per unit  $\ell$ .

Measurements made at Prestwold Hall during 1988 proved the most complete guide to daminozide/adjuvant effects on *V. faba*. Thus, initial consideration of these results may allow a fuller interpretation of investigations in previous seasons. No treatments influenced phytomass partitioning within the pods ( $p = 0.17$ ) and  $\rho_s = 0.79$  (0.0014 SE, with a regression of seed dry weight upon husk weight yielding a slope of 3.73 (SE  $\pm 0.311$ ) with  $p < 0.0001$  and  $R^2 = 0.996$  ( $n = 60$ )). That  $\rho_s$  is a constant for a given genotype in a given season has been measured before.<sup>12</sup> Similarly, total biomass production was unaffected by treatment with varying daminozide-adjuvant combinations ( $p = 0.74$ , Table 1). Daminozide significantly influenced  $\rho_p$  ( $p < 0.001$ ) in an asymptotic relationship to the rate of daminozide applied (Figure 1). Daminozide also increased lodging ( $\ell$ ), such that rates above 2.5 kg of Dazide alone per hectare, with Hyspray or Actipron, or above 1.5 kg of Dazide per hectare with LI700 significantly ( $p < 0.0001$ ) increased  $\ell$  (Table 2).

It is clear that daminozide applied to *V. faba* increased both  $\rho_p$  and  $\ell$  in proportion to the dose rate and that the former will act to increase  $\gamma_s$ , while the latter may have a deleterious effect, depending on the behavior of  $\alpha$  (Equation 1).  $\gamma_s$  was strongly linearly correlated to  $\rho_p$ , where  $\gamma_s/\rho_p = 0.102$  ( $\pm 0.0007$  SE) with  $R^2 = 0.999$ ,  $n = 20$ , and  $p < 0.001$ , suggesting that increased  $\ell$  may affect  $\gamma_s$  by decreasing  $\rho_p$ , thus, at least partially, linking the variables in Equation 1.

From values for spray solution transmitted through the canopy ( $\tau$ ), the proportion of daminozide retained ( $f$ ) could be estimated as  $f = 1 - \tau$ .  $f$  was not affected by either dose rate ( $p = 0.94$ ,  $\bar{f} = 0.88 \pm 0.01$  SE) or adjuvant type ( $p = 0.97$ ). Thus, choice of adjuvant had no effect on spray retention by the canopy. Stevens and Bukovac<sup>34</sup> determined that the uptake of daminozide in aqueous solution in a protected environment was not related to spray application variables, but to the dose retained by the foliage. While their equations only account for the 24 h postapplication period, much of the total uptake of spray occurred during the initial drying period.<sup>33</sup> While Dazide contains 2.8% Triton® X-100 wetter, the resultant surfactant concentration in the spray solution of  $1.4 \times 10^{-4}\%$  (w/w) was considered



TABLE 1  
Seed Yields and Biomass Measured Following  
85% Daminozide (Dazide) Applications to *V.  
faba* at Prestwold Hall During 1988 (n = 60)

Dazide (kg ha <sup>-1</sup> )	Adjuvant			
	None	Hyspray	LI700	Actipron
Seed Yield (t ha <sup>-1</sup> @ 85% DM)				
0	5.01	5.02	4.97	4.87
0.5	5.06	5.24	5.60	5.22
1.5	5.30	5.51	5.98	5.55
2.5	5.56	5.81	5.98	5.92
4.0	6.01	5.78	5.90	5.94

SE = 0.052

	Biomass (g m <sup>-2</sup> DM)			
0	1095	1089	1109	1115
0.5	1166	1068	1103	1044
1.5	1136	1132	1086	1089
2.5	1142	1075	1170	1095
4.0	1064	1096	1126	1082

SE = 12.26

to be negligible, especially due to the poor performance of much higher rates of wetter as alkyl phenol ethylene oxide condensate with daminozide in this and other studies.<sup>4</sup>

Stevens and Bukovac<sup>34</sup> suggested the following equation for the amount of daminozide absorbed ( $\delta_a$ ):

$$\log \delta_a = \log \delta_r \cdot 1.02 - 1.08 \quad (r^2 = 0.93) \quad (2)$$

where  $\delta_r$  is the daminozide retained by the foliage. In this study, calculating  $\delta_r$  as 0.85 Dazide applied and multiplying by  $f$ ,  $\delta_a$  was calculated for the controls, giving a relative indication of absorption if not a definitive absolute value.

Figure 2 shows the relationship between  $\rho_p$  and  $\delta_a$  when no adjuvant was added. A least-squares regression yielded

$$\rho_p = 0.467 (\pm 0.012SE) + 4.6 (\pm 0.8SE) \delta_a \quad (3)$$

where  $\delta_a$  is in kilograms of daminozide per hectare. Using the relationship in Figure 2, the technique of bioassay, common to exogenous and endogenous growth regulator rate assessments, can be evoked by rearranging Equation 3 to give  $\delta_a$  in terms of  $\rho_p$ . For treatments where adjuvants were applied and rates of  $\delta$  gave  $\ell = 0$ , complications arising from  $\rho_p$ - $\ell$  interactions could be avoided. The effects of adjuvants on  $\rho_p$  would be a function of enhanced daminozide uptake or translocation. However, as translocation was principally a function of  $\delta_a$ ,<sup>34</sup> measurements of  $\rho_p$  could be assumed to be dependent on adjuvants affecting daminozide absorption, and not the direct effects of translocation.

Table 3 gives the estimated uptake of daminozide with each of the adjuvants tested. Adjuvants increased the estimated uptake of daminozide, with LI700 showing the largest enhancement, followed by Actipron and Hyspray. At 0.425 kg of daminozide per hectare,

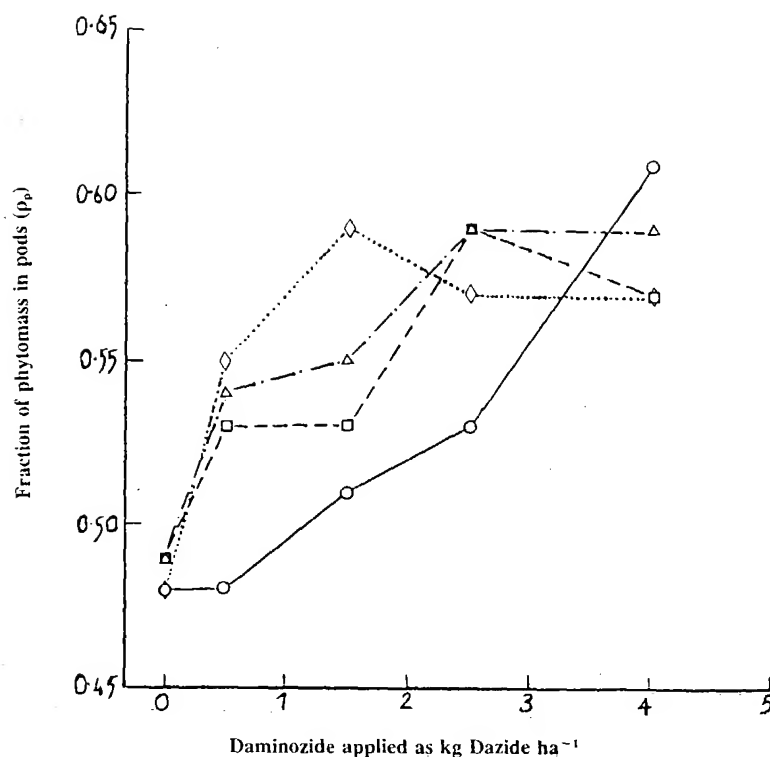


FIGURE 1. Proportion of total plant biomass present as pods (seeds and husks) at harvest related to the dose rate of 85% daminozide (Dazide) applied to the *V. faba* stand at Prestwold in 1988 with no adjuvant (—○—), Hyspray (---□---), LI700 (....◇....), or Actipron (-.-△-.).

TABLE 2  
Percentage Area of Crop Lodged Following  
85% Daminozide (Dazide) Application to *V. faba*  
at Prestwold Hall During 1988 (n = 60)

Dazide (kg ha <sup>-1</sup> )	Adjuvant			
	None	Hyspray	LI700	Actipron
0	0	0	0	0
0.5	0	0	0	0
1.5	0	0	0	0
2.5	0	0	16	0
4.0	21	17	21	13

SE = 1.001

differences between adjuvants were less marked with Hyspray and Actipron (a potential fivefold increase) with LI700 suggesting a sixfold increase in uptake.

At Saxelby Park, daminozide increased  $\ell$  more dramatically than at Prestwold Hall (Table 4). Measurements dividing residual vegetative biomass into leafy tops and vegetative bases indicated that changes in  $p_p$  in favor of the pods arose from a relocation of vegetative biomass below the uppermost podded node, indicating that increased lodging derives from stem emaciation (Table 4).

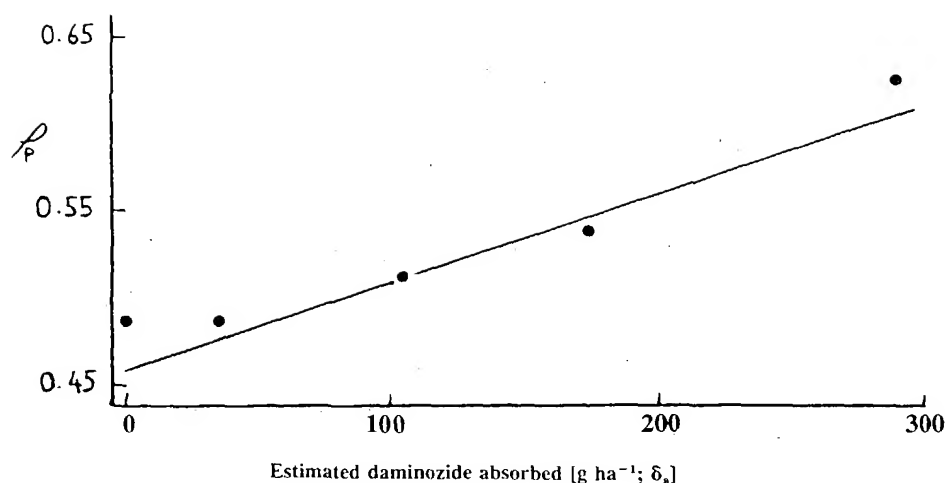


FIGURE 2. Relationship between the proportion of phytomass apportioned into pods ( $p_p$ ) for *V. faba* against the estimated uptake of daminozide ( $\delta_a$ ) described by an imposed linear correlation for the 1988 experiment where no adjuvants were admixed with the spray solution.

TABLE 3  
Estimated Absorption of  
Daminozide ( $\delta_a$ ; g ha<sup>-1</sup>) for *Vicia*  
*faba* Treated with Various  
Adjuvants Admixed in the Spray  
Solution at Prestwold Hall in 1988

Adjuvant	Daminozide (kg ha <sup>-1</sup> )		
	0.425	1.275	2.125
None	30	93	157
Hyspray	137	137	259
LI700	180	273	*
Actipron	159	180	287

Note: Absorption calculated by Bioassay using  $p_p$  when  $\ell = 0$  from Equation 3.

\*  $\ell > 0$ .

Lodging was measured on six occasions between July 1 ( $\ell = 0$ ) and harvest (September 23, where  $0 > \ell \leq 100$ ). A single figure for lodging was derived as the trapezoidal integral of  $\ell$  upon time over the period measured, where  $\int \ell < 30\%$  d. If the physiological mechanism for daminozide/adjuvant-induced changes in  $p_p$  occurred from a relocated stem (directed or stored assimilated) then the change in pod weight ( $\Delta P_w$ ) from daminozide treatment is governed by

$$P_w = \Delta M_v \cdot \epsilon \quad (4)$$

where  $\Delta M_v$  is the change in basal, vegetative phytomass in treated crops over the control and  $\epsilon$  is the efficiency by which  $\Delta M_v$  is directed toward the pods.

TABLE 4  
Applying 85% Daminozide (Alar) to *V. faba* at Saxelby Park During  
1987; Influence on Biomass Production and Partition

Alar (kg ha <sup>-1</sup> )	Adjuvant (0.5%, v/v <sup>-1</sup> )	Vegetative weight				
		Biomass (t ha <sup>-1</sup> )	Top (g m <sup>-2</sup> )	Basal (g m <sup>-2</sup> )	$\rho_p^a$ (%)	$\ell^b$ (%)
0	0	12.2	123	556	44.4	0
0.5	0	12.1	151	473	48.6	0
1.0	0	12.0	132	467	47.2	3
1.5	0	11.8	121	463	50.5	33
2.0	0	12.3	131	554	44.3	m.d. <sup>c</sup>
3.0	0	11.5	122	545	42.0	90
0	LI700	12.2	125	527	46.4	0
0.5	LI700	11.9	125	441	52.5	0
1.0	LI700	11.9	128	476	49.1	40
1.5	LI700	11.6	129	504	45.6	60
2.0	LI700	11.3	120	487	46.3	45
3.0	LI700	11.7	122	568	40.9	100
SE		0.62	15.0	61.1	0.645 <sup>d</sup>	9.7 <sup>d</sup>

<sup>a</sup>  $\rho_p$  = pod weight/biomass.

<sup>b</sup>  $\ell$  = % area of crop lodged; August 12, 1988.

<sup>c</sup> m.d. = missing data.

<sup>d</sup> Backtransformed from logits.

Figure 3 shows that increases in  $\ell$  diminished the effect of daminozide on  $\rho_p$  by reducing both  $\epsilon$  ( $\epsilon = 80.4 [\pm 16.1 \text{ SE}] - 5.59 [\pm 1.59 \text{ SE}] \cdot f\ell$ ;  $p = 0.012$ ,  $\text{SE} = 25.3$ ) and  $\Delta M_v$  ( $\Delta M_v = 109.3 [\pm 10.37 \text{ SE}] - 4.2 [\pm 0.77 \text{ SE}] \cdot f\ell$ ;  $p = 0.001$ ,  $\text{SE} = 19.1$ ), where missing values or those  $\rightarrow \infty$  are absent from the regression.  $\epsilon$  declines to 0 when  $f\ell \approx 14\%$  d. Both Table 4 and the displacement of symbols in Figure 3 show the extent to which daminozide-induced effects were enhanced by adding LI700 to the spray solution.

Figure 4 relates seed yield to applied daminozide. In each case, a parabolic response is evident, the maxima determined by the degree of lodging. In 1986, where lodging occurred only when 4 kg of Alar per hectare was applied, the response was virtually asymptotic. With minimum lodging the response of  $\gamma_s$  to  $\delta$  was around 20% (1986, 1988). However, where lodging was extreme during 1987 ( $0 < \ell < 100\%$  by harvest in all treated plots), the maximum yield response was only 13%.

#### IV. DISCUSSION

As  $\gamma_s$  is directly related to  $\rho_p$ , and daminozide affects  $\rho_p$  in *V. faba* both directly and indirectly by increasing  $\ell$ , Equation 1 can be rewritten,

$$\gamma_s = M_o \cdot \rho_s \cdot \rho_p \quad (5)$$

where  $M_o$  will be a function of edaphic, environmental, and husbandry requisites and  $\rho_s$  is a constant. Further, the influence of absorbed daminozide on  $\rho_p$  can be rewritten,

$$\rho_p = \begin{cases} \rho_p (\text{untreated}) + \gamma_1 \delta_a & \delta_a \leq \delta_e \\ \rho_p (\text{untreated}) + \gamma_2 \delta_a \cdot (1 - \ell \alpha') & \delta_a > \delta_e \end{cases} \quad (6a)$$

$$(6b)$$

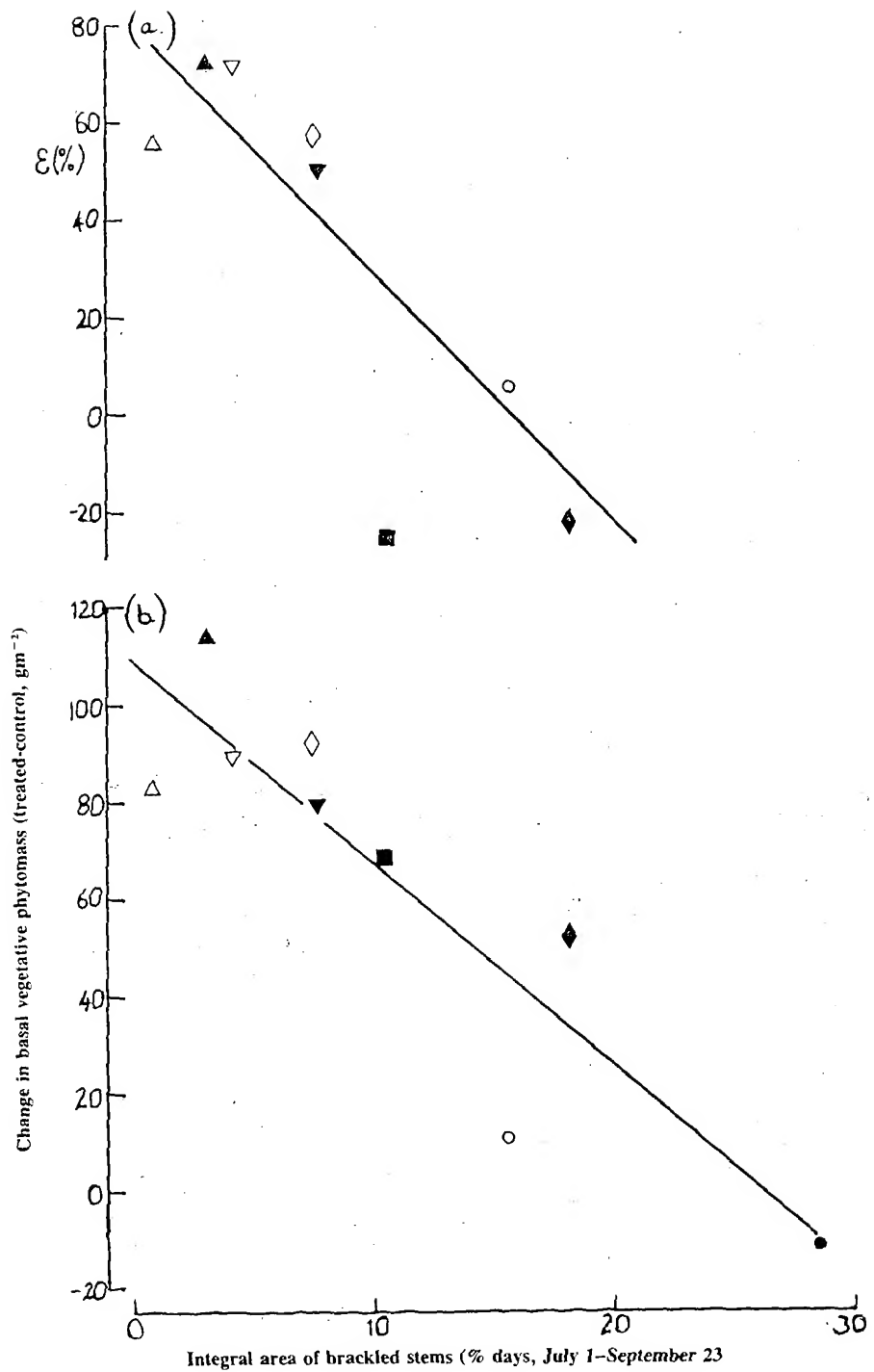


FIGURE 3. Influence of induced lodging on changes in (a) efficiency of relocation of vegetative phytomass into pods ( $\epsilon$ ) and (b) basal vegetative phytomass for *V. faba* grown at Saxelby Park during 1987 following daminozide (Alar) applied at 0.5 (▲, △), 1.0 (▼, ▽), 1.5 (◆, ◇), 2.0 (■, □), and 3.0 (●, ○) kg ha<sup>-1</sup> with (closed symbols) or without (open symbols) LI700 admixed as an adjuvant.



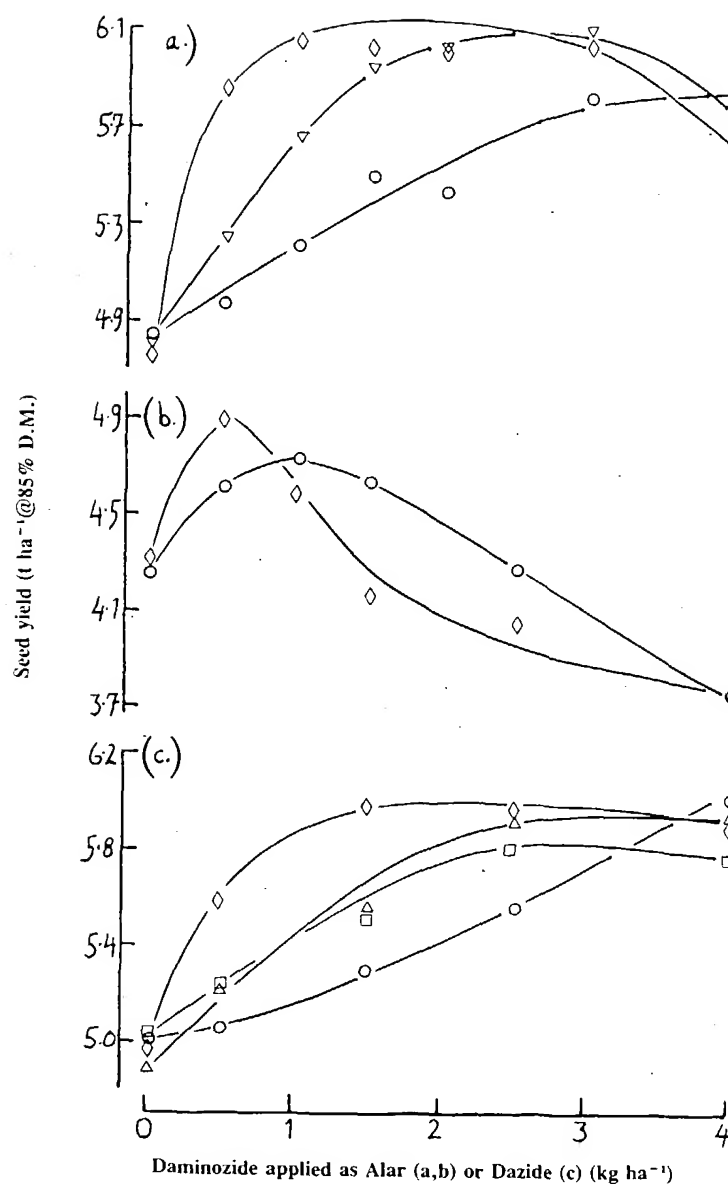


FIGURE 4. Seed yield for *V. faba* following application of Alar in 1986 [a] and 1987 [b] and Dazide in 1988 [c] without an adjuvant (○) or with Agral (▽), Hyspray (□), LI700 (◇), or Actipron (△). Curves drawn by eye.

where  $\delta_c$  is  $\delta_a$  when  $\ell > 0$ ,  $\gamma_1$  and  $\gamma_2$  are the rate of increase of  $\rho_p$  per unit  $\delta_a$ , and  $\alpha'$  is the fractional reduction of  $\rho_p$  per unit  $\ell$ . Now, if

$$\delta_a = 10^{\beta_1 \cdot \log(\delta \cdot [1 - \tau]) - \beta_0} \quad (7)$$

$\beta_1$  will be the slope of a regression of  $\log \delta_a$  upon  $\log \delta_r (= \log \delta \cdot [1 - \tau])$  with  $\beta_0$  as its intercept, i.e., where no adjuvant is used,  $\beta_1 = 1.02$  and  $\beta_0 = 1.08$ .<sup>31</sup>

We may consider the relationship between  $\rho_p$  (thus,  $\gamma_2$ ) and  $\delta$  to be an addition of two separate functions, one relating to  $\rho_p$  to  $\delta$  in the absence of lodging. This will be a function

of  $p_p$  on  $\delta$ , allowed for by combining Equations 6a and 7. When  $\delta_a > \delta_c$ , lodging is underway and will increase with the rate of daminozide (Table 2), and  $\ell\alpha'$  (Equation 6b) will increase to dominance (the maximum); hence, the relationship between  $p_p$  and  $\delta$  will be of negative slope.

Of agronomic import are the factors influencing both the response to daminozide and the level of  $\delta$  when  $p_p$  is maximal ( $\delta_{opt}$ ). It follows from Equations 6 and 7 that  $\gamma$ ,  $\alpha'$ ,  $\ell$ ,  $\delta_c$ ,  $\tau$ , and  $\beta_1$  will all be important in this respect.

Rate of response to  $\delta$  ( $\gamma$ ) and crop response to lodging ( $\alpha'$ ) will be subject to genotypic and environmental variance. The degree of lodging will be affected by environmental husbandry factors that influence  $\ell$ . For example, if lodging pressure is high due to the culture of tall cultivars,<sup>5</sup> high preflowering water supply,<sup>14</sup> or warm nights,<sup>30</sup> then low rates of  $\delta_a$  may cause severe lodging and  $\delta_{opt}$  will be low. If  $\ell$  can be controlled, then  $\delta_c$  may be high and  $\delta_{opt}$  may be a function of the relationship between  $p_p$  and  $\delta_a$  alone (Equations 6a and 7).

Potentially, spray adjuvants may affect the retention of  $\delta$  by the canopy (reducing  $\tau$ ) by achieving adherence and rainfastness. None of the adjuvants tested in 1988 achieved this;  $\tau$  was unchanged. Alternatively, adjuvants may affect the rate of uptake,  $\beta_1$ . Regressing the estimated uptake for 1988 (Table 3), when  $\ell = 0$ , upon  $\delta_c$  through  $\beta_0 = 1.08$  gives  $\beta_1$  for Hyspray = 1.11 ( $\pm 0.058$  SE;  $p = 0.003$ ,  $R^2 = 0.994$ ), LI700 = 1.22 ( $\pm 0.072$  SE;  $p = 0.038$ ,  $R^2 = 0.996$ ), and Actipron = 1.14 ( $\pm 0.058$  SE;  $p = 0.003$ ,  $R^2 = 0.995$ ).<sup>34</sup> Of interest is the mechanism by which LI700 increases the analogous rate parameter for daminozide uptake by 13% compared to around 5% for the mineral oil and tallow amine. Similar increases in efficacy have been recorded following the addition of LI700 to an aqueous solution of mepiquat chloride with 2-chloroethyl phosphonic acid.<sup>13</sup>

We may conjecture that this is not a result of changes in surface deposition when all resultant spray solutions will have aqueous surface tensions of around 30 to 35 dyn cm<sup>-1</sup>. Additionally, *V. faba* leaves are easily wetted.<sup>21</sup> Further, microabrasion of epicuticular wax in field crops may negate surfactant enhancement of uptake in the field.<sup>2,8,9,31</sup> Alterations to electronegative gradients using propionic acid, the influence of phosphoglyceride as a plasmalemma constituent, the influence of free protons on proton pumps, or the modification of plasmalemma ATPase by protons or surfactants are all possibilities worthy of consideration in future studies.<sup>16,26</sup> If tenable, modifications to translocation in addition to uptake are equally plausible. Increased movement of difenzoquat from *Vicia* leaves following the addition of linear alcohol ethoxylate has been reported by Holloway and James.<sup>17</sup> Increasing translocation and decreasing chemical binding,<sup>27</sup> cuticular retention, or epidermal storage could in turn enhance uptake by increasing the concentration gradient for diffusion in Fick's first law as modified by Nobel.<sup>24,28,35</sup> This suggests that uptake may be dependent on translocation away from the site of entry rather than the converse.

## V. CONCLUSIONS

Increasing the dose rate of daminozide to crops of *V. faba* showed a two-phase response. Initially, daminozide increased the proportion of phytomass in pods by reallocating matter found in basal vegetative plant parts for untreated crops. High rates of daminozide induced lodging which, when greater than a threshold value, caused  $p_p$  to decline. The maxima of a parabolic relationship to  $\gamma$ , upon  $\delta$  in 3 years of study varied due to the choice of adjuvant (Figure 4). Acidified soyal lecithin, tallow amines, ethylene oxide condensate wetters, and emulsified mineral oil all increased the rate of response and the degree of lodging and reduced  $\delta_{opt}$  over daminozide applied as Alar or Dazide. LI700 was consistently the most effective adjuvant tried, and further study should determine whether this is due to direct or indirect effects on uptake caused by possible increases in translocation.

Seed yield was directly related to  $p_p$ , and in the absence of severe lodging, yield increases of up to 25% were recorded. It is of interest that changes in phytomass fractionation in favor of yielding organs is the mechanism for daminozide-induced yield responses in *Daucus carota* and *Raphanus sativus*.<sup>6,8,36</sup> Such interspecies communality to responses of exogenous regulators is uncommon, and adjuvants will have an important role to play in achieving improved consistency.

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## Chapter 57

THE USE OF SPRAY ADJUVANTS IN BARLEY-GROWING  
PROGRAMS IN SCOTLAND

K. P. Dawson

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## ABSTRACT

Trials carried out during 1988 and 1989 have clearly shown the benefit of two spray adjuvants in achieving more reliable results from a spray program in barley. In 18 trials in 1988 and 1989, over a range of sites and cultivars, the addition of a phospholipid adjuvant (PA) to a program of autumn- and spring-applied pesticides and growth regulators gave a mean yield increase of 0.39 t/ha. Yield increases were due to increases in ear numbers and mean grain weight, which varied with variety and site. This yield increase equated to a three-fold return on adjuvant cost. The addition of a synthetic latex (SL) to the first node spray in three trials significantly increased yield by 0.44 t/ha. This yield increase equated to a 20-fold return on adjuvant cost. The yield from plots which were artificially wetted to simulate heavy dew was higher than in untreated plots where no adjuvant was applied. In further trials, uptake of manganese was significantly increased by the addition of the PA from a mean of 65 ppm 10 DAT to 122 ppm 20 DAT.

These adjuvants offer hope for improving the reliability of targeting, increasing the window of opportunity for spray applications, and the possibility of reducing the rates of pesticides while maintaining yields and gross margin.

## I. INTRODUCTION

Cool, wet weather and difficult disease patterns in the major barley-growing areas of the North produce problems for the grower in achieving reliable uptake of growth regulators, trace elements, and systemic fungicides. Suitable opportunities to spray crops are at a premium, particularly in the autumn and early spring, as the unstable weather conditions can reduce drying time for applications below that stipulated by manufacturers' label recommendations. Previous work by Dawson and Hutcheon<sup>1</sup> and Jordan and Stinchcombe<sup>3</sup> has shown that integrated production systems offer the most reliable return for the grower. This requires tank mixing of several chemicals and nutrients to optimize the use of good spraying conditions.

Previous work by Green et al.<sup>2</sup> and Percival et al.<sup>5</sup> has clearly shown improvements in uptake and crop effect with the addition of soya lecithin acidified with propionic acid with growth regulators in cereals. The aim of the current trials was to investigate opportunities for the use of two specific spray adjuvants to improve or maintain responses to specific crop treatments under field conditions in northern Britain in a commercial production program. Much of the previous work on adjuvants has been carried out with technical active ingredients, rather than commercial formulations, on greenhouse-grown plants where wax and cuticle dynamics may differ markedly from field conditions and disease and cuticle abrasion may affect the uptake. Thus, the differences in greenhouse work and the use of single compounds and adjuvants require substantive evidence from field trials using a commercial program and more complex tank mixes.

## II. MATERIALS AND METHODS

Trials were sited at three locations in northern Britain at Kelso (Borders Region), Aberdour (Fife Region), and Mintlaw and Elgin (Grampian Region) on both spring and winter barley during 1988 and 1989. All sites were plowed and fertilized to advisory recommendations prior to drilling. Winter barley trials were sown at Kelso on September 24; Aberdour on September 23; and Mintlaw on October 2, 1987. In 1988, they were sown on September 16, 18, and 20, respectively. The trials of spring barley were sown at Aberdour on March 31, 1988, and at Elgin (Grampian Region) and Kelso (Borders Region) on April 2 and 4, 1989, respectively.

The trials were a randomized block design with four replicates. Barley was sown at between 450 and 550 seeds per square meter, depending on the cultivar. Plot size was 12 m by 2 m, and plots were sprayed with an Azo® small-plot sprayer using flat fan 80° E02-80 nozzles at 2.5 bar and 250 l/ha water volume, producing a medium spray quality.

The standard growing program details are shown in Table 1. Tiller and ear numbers were calculated as the mean of four 0.1-m<sup>2</sup> circular plats per plot with four replicate plots per treatment. The plots were harvested with a Claas Compact small-plot combine and yields corrected to 15% moisture content. Throughout the season, the top three leaves were assessed for disease, and at harvest, the levels of necking (collapse of peduncle) and brackling (lodging) of the straw was assessed. At one site, ear loss was assessed using ten 0.1-m<sup>2</sup> circular plats per plot, with four replicate plots per treatment. The growth stages quoted are those of the decimal, growth stage scale.<sup>6</sup> Apart from relevant experimental treatments, trace elements were applied to the plots in response to soil and tissue analysis. Soil pH was in the range of 5.9 to 6.4. Manganese tissue was analyzed by nitroperchloric acid digestion followed by atomic adsorption, after prewashing the foliage with distilled water.

The following fungicides were used in the crop protection program: fenpropimorph (750 g of active ingredient (a.i.) per liter), tridemorph + triadimenol (375 + 125 g a.i./l); prochloraz (400 g a.i./l); chlorothalonil (500 g a.i./l); and propiconazole (250 g a.i./l). The following growth regulators were used: chlormequat chloride (645 g a.i./l) and 2-chloroethylphosphonic acid + mepiquat chloride (155 + 305 g a.i./l). Many of these products contain their own wetter systems to improve their spraying characteristics, and so are deemed by manufacturers to be adequately wetted for normal conditions, especially a tank mix with other formulated products.

Three particular subjects were investigated as follows:

- Experiment 1 the effect of PA in tank mixtures during the autumn and early spring in winter barley
- Experiment 2 the effect of SL in tank mixtures in early spring in winter barley on crops with differing leaf wetness
- Experiment 3 the effect of PA on the uptake of manganese in spring barley

#### A. DETAILS OF ADJUVANTS

The following adjuvants were studied: acidified (propionic acid) soyal phospholipids (principally lecithin, phosphatidyl inositol, phosphatidyl choline, phosphatidyl ethanolamine, and phosphatidyl serine) esterified with four higher fatty acids at 750 g of phospholipid per ha (as 1.0 l/ha of LI700, Loveland Industries Inc.), equating to 0.4% (v/v) of spray solution (PA), and synthetic latex, 63 g/ha (as 0.2 l/ha of Bond®, Loveland Industries Inc.), equating to 0.08% (v/v) of spray (SL).

#### B. PHOSPHOLIPID ADJUVANT WITH AUTUMN AND SPRING TANK MIXES

In experiment 1, the addition of PA to tank mixtures was examined. Treatments were the standard program with and without PA in the GS13 + 23 + 31 sprays (autumn + spring) or with the 23 + 31 sprays only (spring only). The autumn + spring applications comparison was examined in 12 trials in 1988, and the spring only in two of these trials, on the varieties cv. Plaisant (6 rows) and cv. Magie (2 rows), four comparisons each, and cv. Gerbel (6 rows) and cvs. Fallon, Igri, and Frolic (2 rows), one comparison each. In 1989, the spring-only comparison was carried out in six trials, three each of cv. Plaisant and cv. Pastoral.

TABLE 1  
Winter Barley-Growing Program, 1988 and 1989

GS 13 November 22		GS 23 March 8		GS 30/31 April 13		GS 37/39 May 14		GS 59 June 12	
Tridemorph	262	Tridemorph	262	Fenprop	375	Ethephon	232	Fenprop	375
Triadimenol	88	Triadimenol	88	Prochloraz	200	Mepiquat	453	Propcole	100
Chlormequat	483	Chlormequat	483	Chlorothal	250	Chloride			
Manganese	65	Manganese	64	Chlormequat	966	Propcole	100		
				Manganese	128				
				Copper	82				

Note: All treatments received 200 kg N/ha in a three-split application system during the spring. Trace elements were EDTA chelates. Rates are g a.i./ha.

### C. USE OF SYNTHETIC LATEX IN RELATION TO LEAF WETNESS

The addition of SL solution to the main spring tank-mix was investigated. Treatments included the standard spray at first node with and without SL on the dry crop surface. In a third treatment, the crop surface was sprayed with water until run-off to establish a leaf wetness, and the tank mixture was applied with SL. Two trials were conducted in 1988 on the varieties cv. Plaisant (6 rows) and cv. Magie (2 rows). Two trials were conducted in 1989 on cv. Pastoral (2 rows).

### D. THE EFFECT OF PHOSPHOLIPID ADJUVANT ON UPTAKE OF MANGANESE

The addition of PA to spray solutions of manganese sulfate (1600 g Mn/ha) and an inorganic dry flowable formulation (300 g/ha) was investigated in spring barley at three sites, one in 1988 and two in 1989. The variety cv. Camargue was used in all three trials. The spray solutions included Tridemorph® (375 g a.i./ha) as a fungicide with a wetter system in the product formulation (Table 1).

## III. RESULTS

### A. PHOSPHOLIPID ADJUVANT WITH AUTUMN AND SPRING TANK MIXES

In 12 trials in 1988 over a range of sites and varieties, the addition of PA to a program of chlormequat chloride applications alone gave a mean yield increase of 0.39 t/ha ( $p < 0.05$ ). This yield increase was due to increases in ear numbers and changes in mean grain weight, which varied with variety and site (Table 2). At one site subject to severe gales immediately prior to harvest, a reduction in ear loss of 0.52 t/ha was evident ( $p < 0.05$ ) in the PA treatment, and a reduction in necking was evident at all sites. There were no differences in disease control between treatments, with the program keeping all treatments at very low disease levels despite a season of fairly high disease pressure (35% mildew in untreated controls). There was no additional benefit to autumn usage of PA compared with usage in the spring alone, and in several trials, yields were reduced. Increases in yield were more strongly correlated with tiller numbers in early May and final ear number than mean grain weight (MGW) at the Fife site, where more detailed measurements were carried out. For the six-row variety, Plaisant, the addition of the adjuvant significantly decreased MGW while increasing harvested yield, presumably through effects not only on increased ear number, but also on grains per ear. For the two row variety, Magie, both ear number and MGW increased. No significant differences in final culm length occurred in the trials, but during the start of stem elongation, the adjuvant-treated plots were noted to be shorter.

TABLE 2  
The Effect of a Phospholipid Adjuvant in Tank Mixtures on Winter Barley at  
Aberdour, 1988

Variety	Time	Yield (%) of control	Ear no. (m <sup>2</sup> )	Tiller no. (m <sup>2</sup> ) May	MGW necking	
					(g × 10 <sup>-3</sup> )	(%)
Plaisant	A + S	105	107	108	92	72
	S	107	109	110	93	70
Control	—	100 (10.48 t/ha)	596	720	41.4	30
Magie	A + S	104	109	115	109	84
	S	105	111	112	112	79
Control	—	100 (9.81 t/ha)	1080	1250	44.4	15
Significance against control	*	*		*	**	**

Note: A + S, autumn + spring PA; S, spring PA only; MGW, mean grain weight; necking, collapse at the peduncle of the plant; \* and \*\*, significant at  $p < 0.05$  and  $p < 0.01$ , respectively

TABLE 3  
The Effect of Synthetic Latex Adjuvant on the  
Yield and Ear Number of Winter Barley Used in  
Tank Mixture at GS 30/31, 1988 and 1989

Treatment	Dry leaf		Wet leaf	
	Yield (t/ha)	Ear no. (per m <sup>2</sup> )	Yield (t/ha)	Ear no. (per m <sup>2</sup> )
Control (no bond)	9.25	865	—	—
Bond	9.70*	831	9.50	820

Note: Mean of four trials; \*, significant at  $p < 0.05$ .

In six trials in 1989 over a range of sites and varieties, the addition of LI700 to a program of spring sprays gave a mean yield increase of 0.42 t/ha ( $p < 0.05$ ).

#### B. USE OF SYNTHETIC LATEX IN RELATION TO LEAF WETNESS

Addition of SL to the first node spray in four trials significantly increased yield by 0.44 t/ha ( $p < 0.05$ ). Where the plots were artificially wetted to simulate heavy dew, the yield was higher than the control without adjuvant, but not significantly (+0.25 t/ha). No differences in disease control were apparent between treatments. The effect was similar with two-row and six-row varieties (Table 3).

#### C. THE EFFECT OF PHOSPHOLIPID ADJUVANT ON UPTAKE OF MANGANESE

Work on manganese uptake in spring barley with and without the adjuvant PA showed that appreciable increases in tissue manganese can be achieved by foliar-applied manganese. The increase in tissue manganese is increased with the addition of the PA. All three trials gave very similar responses, and hence are arranged (Table 4).

Both forms of manganese increased tissue manganese above the deficient action threshold (30 ppm). The increase in tissue manganese was not directly related to the absolute amount of manganese applied. In terms of efficiency, the inorganic dry, flowable formulation was



TABLE 4  
The Effect of LI700 on the Uptake (ppm) of Two  
Forms of Manganese, 10 and 20 DAT

Adjuvant	Inorganic dry flowable		Manganese sulfate		Control LSD	
	-	+	-	+	-	+
10 DAT	49	100	80	144	32	25
20 DAT	22	40	54	81	19	15
Mean applied (g/ha)	300	300	1600	1600	0	—

Note: Mean of three trials, 1988 and 1989; LSD, least significant difference.

better than manganese sulfate. For both manganese forms, the adjuvant improved the efficiency of uptake significantly 10 and 20 d after treatment. The inorganic dry flowable without the adjuvant dropped below the deficiency threshold by 20 d after treatment and was not significantly different from the control. The increase in yield attributable to the adjuvant over manganese alone in 1988 was 0.25 t/ha. No differences in yield were exhibited in 1989, although large differences in green leaf area were evident with addition of PA. It is probable that these differences were not reflected in yield due to the dry summer.

#### IV. DISCUSSION

Benefits of the PA for yield improvement through improved spray targeting translated from the laboratory to the field in a commercial growing program. Significant changes in tiller and ear numbers, together with ear loss and necking differences suggested improved uptake of chlormequat.<sup>4</sup> This together with transient effects on crop height suggest that despite the tank mixture being composed of commercial products, each with its own wetter system, the PA provided an additional effect on uptake. This was also indicated by the work on manganese uptake where a commercial formulation of fungicide with its own wetter was applied in a tank mixture, but increases in uptake were still achieved by using PA.

Synthetic latex trials showed that despite the drying of the spray solution onto the dry leaf without the latex adjuvant, the latex still improved spray performance. The mechanism is unclear, but two possibilities are enhanced retention and/or a change in droplet spectrum. Enhancement provided by the adjuvant on the wet leaf surface suggests that retention is the more likely mechanism, but further work is required to elucidate the mechanism.

Field trials show clearly that economic and environmental benefits can be gained in a commercial barley-growing program with the use of LI700 and Bond. The adjuvants offer scope for improving reliability of, and increasing the window of opportunity for spray application, hence reducing the costs and environmental damage by poor targeting or agri-chemical sprays.



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## Chapter 58

**THE INFLUENCE OF AN ADJUVANT ON THE RESPONSE OF  
WINTER BARLEY TO THE GROWTH REGULATOR  
CHLORMEQUAT**

R. H. Newman

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## I. INTRODUCTION

Chlormequat (2-chloroethyl triethylammonium chloride) is widely used as a growth regulator in winter barley (*Hordeum distichon*) in the U.K. The primary reason for its use is to reduce yield losses, harvesting difficulties, and drying costs caused by crop lodging, by shortening and strengthening the lower stem internodes. Recommended stages for application of chlormequat are from mid-tillering to just prior to detection of the first node.<sup>4</sup>

Chlormequat may also increase crop yield in the absence of lodging, through developmental manipulation. To maximize this effect, application should be made at the glume primordia initiation stage of the main stem apical meristem,<sup>6</sup> or glume/lemma primordial initiation stage.<sup>3</sup> In most seasons in the U.K., this will require an application from February to early April, depending on location, cultivar, and sowing date.

The maximum and minimum 30-year average (1951 to 1980) temperature for March in England and Wales are 8.9 and 1.6°C, respectively, with a mean of 5.3°C (Meteorological Office 1989). The minimum air temperature for New 5C Cycocel® (Cynamid's chlormequat formulation) to be effective is around 8°C.<sup>2</sup>

Although spring applications of chlormequat on barley have given small increases outside the benefits from lodging control, the reliability of this increase may not always be sufficient to justify the use of chlormequat for yield promotion alone.<sup>1</sup>

LI 700, an adjuvant based on acidified soyal lecithin, increased the effect of the plant growth regulator combination, ethephon with mepiquat chloride (as Terpal®, BASF) on winter barley.<sup>5</sup> In addition, LI 700 improved chlormequat uptake into leaves of barley and wheat at temperatures as low as 4°C,<sup>7</sup> and initial field trials at the glume primordia stage on winter barley doubled the yield response to chlormequat alone.<sup>6</sup>

## II. MATERIALS AND METHODS

To evaluate further the benefits of using the adjuvant LI 700 to increase the effect of an early application of chlormequat, field investigations were conducted in Scotland by the East of Scotland College of Agriculture (ESCA), and in England by the Agricultural Development and Advisory Service (ADAS) of the Ministry of Agriculture, Fisheries and Food (MAFF). Coincidentally, Arable Research Centres (ARCs) conducted a similar series of field trials in 1988 at three centers in the east and south of England.

Trial details of the five sites appear in Table 1. Chlormequat used in all five trials was Cyanamid's New 5C Cycocel, an aqueous solution containing 645 g/l chlormequat.

Application at the ESCA and ADAS trials was at glume primordium initiation. In the ARC trials, application was slightly later, at the early maximum primordia or maximum primordia growth stage.

All plots at each site received a standard and identical crop protection program.

## III. RESULTS

The yield results are presented in Table 2.

At four of the sites — Berwickshire, Tyne and Wear, Kent, and Hampshire — no lodging was recorded at harvest. At the fifth site, in Cambridgeshire, very slight lodging was recorded just prior to harvest, with 80% of the stems on the untreated plots leaning up to a maximum of 20° from the vertical.

At two of the sites, Tyne and Wear and Cambridgeshire, the use of chlormequat alone gave a significant ( $p = 0.05$ ) yield increase over the untreated plots. At three sites, chlor-

TABLE 1  
Trial Details

Trial details	ESCA	ADAS	ARC	ARC	ARC
Site (county)	Berwickshire	Tyne and Wear	Kent	Cambridgeshire	Hampshire
Variety	Plaisant	Nevada	Fallon	Fallon	Mimosa
Date of drilling	September 19	October 14	September 29	October 23	September 25
Date of trial treatment	March 7	March 20	March 21	April 11	April 13
Growth stage at application	Glume primordia	Glume primordia	Early maximum primordia	Maximum primordia	Maximum primordia
Rate of 5C chlormequat application (l/ha)	2.5	2.5	1.25	1.25	1.25
Date of harvest	August 4	August 3	July 31	July 26	N/A
Lodging (%) and severity on untreated	Nil	Nil	Nil	80/1	Nil

Note: ESCA, East of Scotland College of Agriculture; ADAS, Agricultural Development and Advisory Service; ARC, Arable Research Centre.

TABLE 2  
Yield Results

Site	Yield (t/ha)			LSD ( $p = 0.05$ )
	Untreated	Chlormequat	Chlormequat + LI 700	
Berwickshire	8.86	8.92	9.97	0.21
Tyne and Wear	5.94	6.34	6.73	0.29
Kent	9.04	9.65	10.4	0.7
Cambridgeshire	8.17	8.69	9.12	0.45
Hampshire	9.38	9.13	9.06	0.57
Mean yield	8.28	8.56	9.06	
Mean response over untreated	—	+0.28	+0.78	

mequat + LI 700 produced crops that significantly ( $p = 0.05$ ) outyielded crops where chlormequat was applied alone.

At one site, Hampshire, both chlormequat alone and with added LI 700 produced a slight but insignificant reduction in yield.

Averaging the yield results from all trials showed that chlormequat alone gave a mean increased yield of 0.28 t/ha, while the addition of LI 700 increased the yield by a further 0.5 t/ha, to give a mean increase over untreated of 0.78 t/ha.

Crop height at harvest was recorded at four sites, in Berwickshire, Tyne and Wear, Cambridgeshire and Hampshire. The results are presented in Table 3.

In the Berwickshire, Tyne and Wear, and Cambridgeshire trials, small height reductions of 0.6 to 3.18%, formulated, were recorded from both treatments (chlormequat alone or plus LI 700). At the Hampshire site, chlormequat alone reduced height by 9 cm (11.2%). With LI 700 added to the chlormequat, a reduction of 15 cm (18.6%) resulted.

TABLE 3  
Crop Height Effects at Harvest

Site	Untreated	Chlormequat		Chlormequat + LI 700	
	Height (cm)	Height (cm)	% height reduction from untreated	Height (cm)	% height reduction from untreated
Berwickshire	100.5	98.5	1.5	98.5	1.5
Tyne and Wear	86	85.5	0.6	83.4	3.1
Cambridgeshire	122	119.6	2.0	118.3	3.1
Hampshire	81	72	11.2	66	18.6

#### IV. DISCUSSION

Meteorological records were not kept at all sites, so it is not possible to relate chlormequat performance, with and without LI 700, to the temperature at the time of application and subsequently.

Results reported herein confirm the findings of Green and Green<sup>6</sup> that the addition of LI 700 to chlormequat, applied at the glume primordia stage, can substantially enhance the effect of chlormequat on barley.

At the two sites where applications were made at the glume primordia stage, Berwickshire and Tyne and Wear, adding LI 700 quadrupled the mean yield response given by chlormequat alone. In Tyne and Wear, it doubled the response, and in Berwickshire, its use resulted in a tenfold increase over that given by chlormequat alone.

At the other sites, application was made at a slightly later growth stage than that suggested by Green and Green.<sup>6</sup> At two of these sites, Kent and Cambridgeshire, the addition of LI-700 resulted in a doubling of the yield response given by chlormequat alone.

The Hampshire results are superficially anomalous. Although no yield response was obtained from either treatment, substantial height reductions were obtained from chlormequat with and without LI 700. This trial was the earliest drilled, the latest treated, and the most southerly of all five sites. It also used a different variety from all other sites. The results strongly suggest that at this site, application was made after the crop had passed the stage where chlormequat affects growth manipulation and into a stage where the main effect is on crop height.

This series of trials has confirmed that LI 700 can have a substantial effect on the performance of chlormequat, in terms of both yield response and height reduction. The time of application seems to be critical, for, as has already been suggested, there appears to be a distinct "cutoff" time in the development of winter barley beyond which yield responses to chlormequat may be sacrificed in favor of height reductions.

Further trials using sequential applications of chlormequat and chlormequat + LI 700 at fortnightly intervals, from mid-February to late April, were laid down in spring 1989.

#### ACKNOWLEDGMENTS

I wish to thank Dr. David Lockhart of ESCA, who supervised the trial at the Berwickshire site, Eric Wooley of ADAS, who supervised the trial at the Tyne and Wear site, Dr. Michael Carver, Director of ARC, and the ARC managers who supervised the trials in Cambridgeshire, Kent, and Hampshire. Thanks are also due to Dr. Christopher Green for reading and commenting on a draft of this manuscript.



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## Chapter 59

**THE INFLUENCE OF ADJUVANT TYPE ON THE RESPONSE OF  
OATS TO THE GROWTH REGULATOR CHLORMEQUAT**

Malcolm H. Leitch

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## ABSTRACT

The influence of an acidified soya phospholipid (Spraymate® LI 700) on the response of oats (*Avena sativa* L.) to the growth regulator chlormequat (2-chloroethyl trimethylammonium chloride) was compared in field experiments with a nonionic alkylphenol ethylene oxide condensate.

Both adjuvants increased the growth-retarding activity of chlormequat by more than 30%. However, the soya phospholipid was shown to extend the longevity of effect of the growth regulator within the crop. In situations of high fertility, significantly greater grain yields, unrelated to lodging control, resulted from the addition of the soya phospholipid rather than the alkylphenol ethylene oxide to the spray solution.

The mechanisms of yield improvement are discussed in relation to possible enhanced growth regulator activity.

## I. INTRODUCTION

The growth regulator chlormequat has been used to produce dwarfing effects in a wide range of crops for almost 30 years. It is effective, to varying degrees, in temperate cereals, reducing stem elongation and increasing resistance to lodging. Varieties of oats currently grown in the U.K. are tall and are susceptible to lodging at relatively low levels of applied N fertilizer, yet have often shown poor and inconsistent responses to the growth regulator.<sup>4,5</sup> However, recent work by the author<sup>8</sup> consistently demonstrated large reductions in stem length over a wide range of situations. It was suggested that the poor responses achieved in earlier studies may have been due, in part, to reduced foliar uptake of the chemical as a result of morphological characteristics peculiar to the oat plant. The presence of minute hairs over the leaf surfaces add to their inherently hydrophobic properties, making them more difficult to wet than those of wheat (*Triticum aestivum* L.) or barley (*Hordeum vulgare* L.). Improved uptake of the retardant by wheat and barley leaves has been reported following the addition of a wetting agent.<sup>1</sup> It is probably that the inconsistency and poor responses of oats to chlormequat in earlier work occurred through the absence of a wetting agent, as in many cases this was not specified.<sup>2,6</sup> Baker and Hunt<sup>1</sup> showed that the nature of the wetting agent itself may influence the uptake of the growth regulator. Chlormequat mixed with commercial fungicide formulations was less readily taken up by the cereal leaves than chlormequat mixed with a wetting agent, despite the fact that the fungicides lowered the surface tension of the solution and altered the waxy cuticle in the same manner. Clearly, the role of wetting agents and adjuvants in such situations is complex. This chapter reports on how two different adjuvants influenced the uptake and consequent effectiveness of chlormequat in oats: (1) a standard nonionic wetting agent, alkylphenol ethylene oxide condensate (Agral®, ICI), and (2) an acidified soya phospholipid (Spraymate LI 700, Newman Agrochemicals).

## II. MATERIALS AND METHODS

Field experiments were conducted over two consecutive seasons, 1986 to 1987 and 1987 to 1988, at the UCW Trefloyne Field Station, Tenby, Dyfed, on a deep, silty loam of the Pembroke series.

Experiment 1 was conducted over both seasons. In 1986-87, treatments of chlormequat + Agral and chlormequat + LI 700 were compared with chlormequat alone. Treatments were applied on May 6 at crop growth stage (GS) 32, as defined by Zadoks et al.<sup>10</sup> The plots had received a single N application of 150 kg/ha at GS 30 (April 16). In 1987-88, this

design was modified to include two N rates of 80 and 160 kg/ha at GS 30 (April 19), while the chlormequat-alone treatment was omitted.

Experiment 2 in 1987-88 only, compared the effect of the two adjuvants on the action of chlormequat when applied over a range of crop growth stages: GS 23 (March 14), GS 30 (April 11), GS 32 (May 11), GS 34 (May 20), and GS 23 + 32. In this experiment, a split rate of N of 50 kg/ha at GS 22 (February 23) + 100 kg/ha at GS 30 (April 19) was applied.

The cultivar Peniarth was used throughout the investigation. Experimental plots were 7 m long by 1.2 m wide, comprising of ten rows at 12-cm spacing, with 50 cm of uncropped discard separating adjacent plots. Each experiment was arranged in a randomized block design with four replicates.

Fertilizer, equivalent to 23, 68, and 68 kg/ha of N,  $P_2O_5$ , and  $K_2O$ , respectively, was applied prior to final seed-bed preparation. The plots were seeded at the rate of 400 seeds per  $m^2$  using an Oyjord plot drill. The residual herbicide methaGenzthiazuron (*N*-(2-benzothiazolyl-*N,N'*-dimethylurea) was applied before crop emergence, after which no further weed control was required. A cypermethrin insecticide was applied during the first week of November to control the aphid vector of barley yellow dwarf virus, and the fungicide propinconazole prior to ear emergence as a precautionary measure to reduce the risk of mildew and crown rust infection.

Fertilizer (N) treatments, given as ammonium nitrate (34.5% N), were applied with a Gandy® fertilizer spreader. Chlormequat treatments were applied using a knapsack sprayer with a hand-held boom 1.25 m in length. A polythene shield was used to prevent drift to adjacent plots. Rate of application was 1610 g of active ingredient (a.i.) per ha in 200 l water per ha with the appropriate adjuvant where required. LI 700 was added at a rate of 5 ml/l spray solution and Agral at a rate of 0.25 ml/l spray solution.

From mid-May onward, measurements of canopy height were made at weekly intervals until the maximum height had been attained, and from mid-July until harvest, assessments were made, as required, of the degree of lodging sustained. Plots were scored according to the percentage of the total area affected and the angle of deviation of the stems from the vertical (0 to 90°), giving a potential maximum lodging score of 9.0 ( $100 \times 90/1000$ ).

At harvest, samples consisting of 4 × 0.5-m lengths of adjacent center rows were cut at ground level in order to record components of yield and to provide an estimate of total yield. Measurements of total stem length were made on a subsample of 20 stems per plot in experiment 1, while in experiment 2 measurements of both total length and individual internode length were made on ten stems per plot. The center 5-m length and entire 1.2-m width of each plot was harvested using a Wintersteiger plot combine harvester to provide an estimate of commercial grain yield.

### III. RESULTS

#### A. EXPERIMENT 1

##### 1. Stem Length and Lodging Control

The effect of chlormequat treatments on the development of canopy height during 1986-87 is shown in Figure 1. Chlormequat alone reduced the final canopy height by 33 cm (18.2%), while the addition of either adjuvant increased the magnitude of responses, reducing the height attained by 44 cm (24.3%), an improvement of some 33%. It appears that the initial suppression of extension growth was similar with or without the inclusion of adjuvants to the spray solution, but that the effect of the chlormequat was more persistent where the adjuvants had been added, increasing its period of activity by approximately 10 to 15 d. Despite the height of the untreated control plots, they suffered only little from lodging

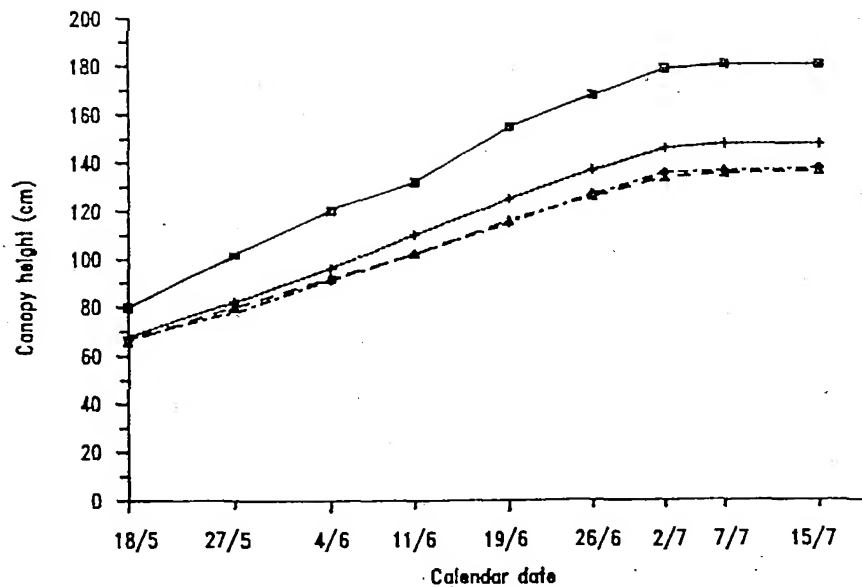


FIGURE 1. Development of winter oat canopy height with time, 1986 to 1987. □—□, untreated; +--+ , chlormequat; ◇-◇, chlormequat + Agral; △-△, chlormequat + LI-700.

(average of 31%), and this was completely controlled by the application of chlormequat with or without the addition of adjuvants. In the following 1987-88 season, the pattern of canopy height development was similar to the previous season, and although the stems were considerably shorter at comparable N rates (average of 35 cm), crop lodging was more severe (Figure 2). At the lower (80 kg/ha) level of applied N, the degree of lodging was similar to that recorded in the previous season, and was again completely controlled by chlormequat irrespective of adjuvant type. At the higher N level (160 kg/ha), lodging at harvest in the untreated controls was at an average of 62%, and although a similar value was recorded in those treatments which had received chlormequat, it was apparent that this lodging occurred later in the season than in the controls. The type of adjuvant added to the spray solution had little effect upon the action of chlormequat.

## 2. Grain Yield.

In 1986-87 and 1987-88 at the higher level of applied N, treatment with chlormequat + LI 700 led to significantly higher grain yields than were achieved from untreated controls or from treatment with chlormequat + Agral (Table 1). The mechanisms of yield improvement differed in successive seasons. In 1986-87, comparison of grain from hand- and combine-harvested samples suggests that the yield benefit was an effect of improved grain filling, resulting in fewer small grains and, consequently, reduced losses during combining, while in 1987-88, it was due to a larger number of panicles per unit area, with grain size remaining largely unaffected. In neither season was the increased yield the result of improved lodging control, since both adjuvants had a similar effect on stem length and resistance to lodging.

## B. EXPERIMENT 2

Figure 3 shows how the different adjuvants influenced the growth retarding activity of chlormequat when applied over a range of crop growth stages. Irrespective of adjuvant, chlormequat was most effective when applied at or after GS 32. Before this growth stage,



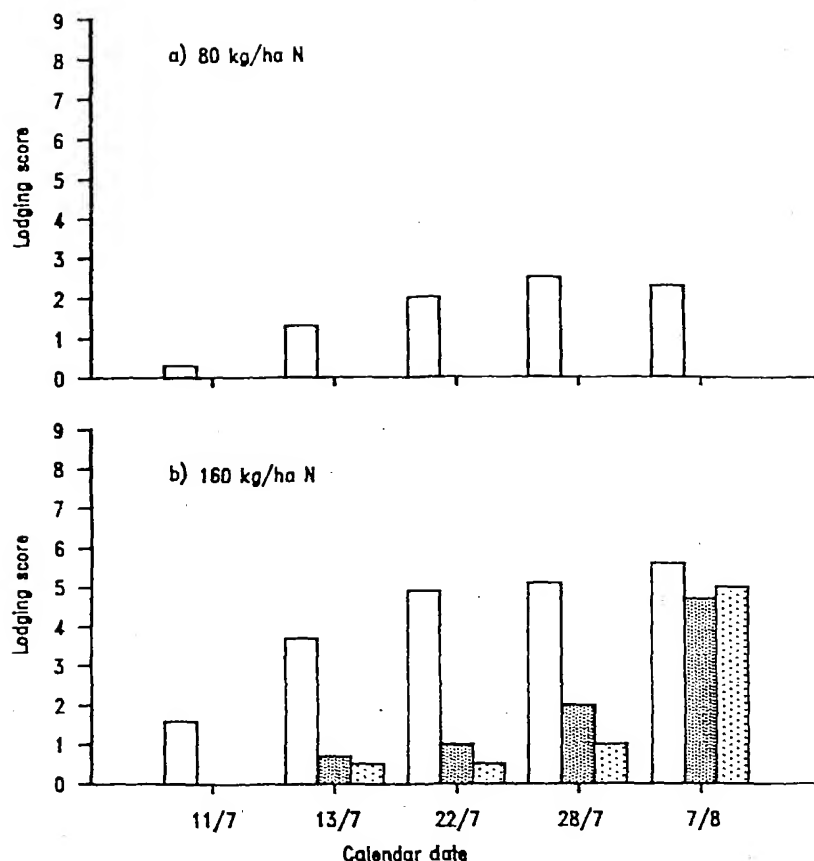


FIGURE 2. Development of lodging with time in winter oats cv. Peniarth, 1987 to 1988, at (a) 80 kg/ha N and (b) 160 kg/ha N.  $\square$ , untreated;  $\text{▨}$ , chlormequat + Agral;  $\text{▩}$ , chlormequat + LI-700.

however, the type of adjuvant added to the spray solution was shown to alter the effectiveness of the growth regulator. At GS 30, the addition of LI 700 resulted in significantly shorter stems than was achieved with the addition of Agral to the chlormequat, while at GS 23 the reverse was true. The degree of lodging sustained was found to be related to final stem length.

In terms of grain production, the largest yields were achieved with chlormequat applied at GS 32, irrespective of adjuvant. These higher yields were associated with a larger number of grains per panicle, despite a decrease in individual grain size, and a small increase in the numbers of panicles per unit area (Table 2).

Measurement of individual stem internodes (Table 3) indicated that progressively later applications of chlormequat shortened progressively later-formed internodes. At the earlier times of application, the influence of adjuvant type could be identified. At GS 23, the addition of LI 700 to the chlormequat resulted in longer lower and middle internodes than were found following the addition of Agral, leading to a greater overall stem length. In contrast, at GS 30, chlormequat + LI 700 significantly reduced the length of the two uppermost internodes. This resulted in a total stem length significantly less than that found following chlormequat + Agral at GS 30, and not greatly different from that obtained from the otherwise more effective GS 32 timing.

## TABLE I

	1986 to 1987			1987 to 1988							
	Chloromequat			S.E.	80 kg/ha N			160 kg/ha N			
	Chloromequat	+ Agral	+ LI 700		Untreated	+ Agral	+ LI 700	Untreated	+ Agral	+ LI 700	
Combine grain yield (t/ha)	10.83	10.98	11.70	0.256	6.10	6.30	6.45	8.48	8.54	9.21	0.223
No. panicles per m <sup>2</sup>	636	621	626	12.3	465	475	471	446	521	526	23.5
Average grain wt (mg)	26.3	27.0	26.4	0.43	27.4	27.1	27.4	28.3	28.0	27.6	0.26
Mean individual*											
Panicle wt (g)	1.64	1.72	1.68	0.061	1.36	1.31	1.37	1.85	1.64	1.68	0.075
Grain wt (mg)	24.1	22.7	26.1	0.62	28.1	27.6	27.3	29.5	28.4	27.3	0.61
Stem length (cm)	—	—	—	—	95	76	78	111	83	84	2.1

<sup>a</sup> Derived from hand-harvested samples.

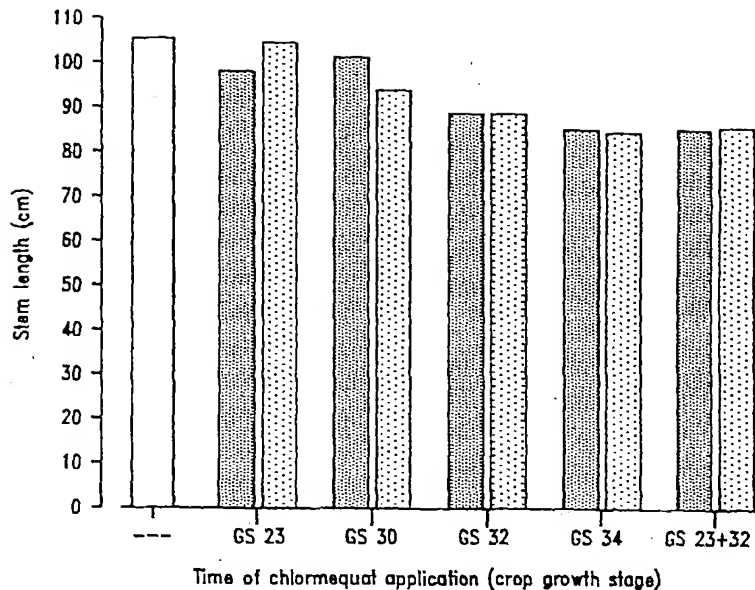


FIGURE 3. Effect of time of chlormequat application on final stem length of winter oats cv. Peniarth in 1987 to 1988. □, untreated; ▨, chlormequat + Agral; ▩, chlormequat + LI-700.

#### IV. DISCUSSION

The growth retarding effect of chlormequat in oats was clearly enhanced by the addition of both adjuvants, and when chlormequat was applied at GS 32, the most effective time of application, the response was unaffected by the type of adjuvant added. Both appeared to increase the persistence of its effect. It is likely that the difficulty in wetting the leaf surface in the absence of an adjuvant limited the amount of chlormequat taken up by individual plants. A more uniform distribution over the leaf surface would have allowed a greater uptake of the growth regulator, which would have resulted in a greater persistence within the plant. This is consistent with the results of Baker and Hunt,<sup>1</sup> who found significant improvement in both retention on the leaf surface and uptake of chlormequat into wheat and barley leaves when Agral 90 was added to the spray solution. In the absence of any lateral movement of chlormequat from the areas of droplet contact, they concluded that increased uptake resulted directly from increased coverage rather than from increased penetration per unit area. It is interesting to note, however, that even at the highest concentration of the adjuvant Agral 90, uptake of chlormequat was only 54% in wheat and 24% in barley. Clearly, there remained considerable capacity for greater uptake of the growth regulator.

In contrast to the results of chlormequat applied at GS 32, the magnitude of crop responses to earlier applications differed significantly as a result of the type of adjuvant added. Applications at both GS 23 and GS 30 indicated a more persistent effect of the growth regulators where LI 700 was added compared with Agral. This may have occurred through increased coverage and/or greater penetration per unit area. At GS 30, this resulted in a greater reduction in stem length. Applied at GS 23, however, the opposite effect was achieved. This negative response to the growth regulator has been observed before, where early applications of chlormequat increased final stem length and reduced resistance to lodging compared with untreated controls.<sup>7,9</sup> It is likely to be the result of the mode of action of chlormequat. While the precise mechanism has yet to be elucidated, it is thought to inhibit gibberellin production,

TABLE 2  
Grain Yield and Components of Yield of Winter Oats cv. Peniarth in 1987-88 Following Treatment with Chlormequat over a Range of Growth Stages

	Growth stage at which chlormequat applied										SE	
	GS 23		GS 30		GS 32		GS 34		GS 23+32			
	+ Agral	+ LI 700	+ Agral	+ LI 700	+ Agral	+ LI 700	+ Agral	+ LI 700	+ Agral	+ LI 700		
Untreated control												
Combine grain yield (t/ha)	7.35	6.99	7.51	7.56	7.33	8.05	8.08	7.49	7.36	7.38	8.08	0.292
No. panicles per m <sup>2</sup> *	503	497	539	476	507	542	522	498	599	423	520	23.9
Mean individual*												
Panicle wt (g)	1.40	1.28	1.39	1.53	1.35	1.58	1.47	1.44	1.29	1.40	1.60	0.013
Grain wt (g)	26.1	26.2	25.6	25.8	24.8	25.5	24.7	25.6	25.2	25.3	24.8	0.39
No. grains per panicle	48	44	49	54	49	57	54	51	47	50	59	3.7

\* Derived from hand harvested samples.

TABLE 3  
Stem Internode Lengths (cm) of Winter Oats cv. Peniarth Following Treatment with Chlormequat over a Range of Growth Stages

Internode	Untreated control	Growth stage at which chlormequat applied										SE
		GS 23		GS 30		GS 32		GS 34		GS 23+32		
		+ Agral	+ LI 700	+ Agral	+ LI 700	+ Agral	+ LI 700	+ Agral	+ LI 700	+ Agral	+ LI 700	
1 (base)	0.7	0.1	0.8	0.6	0.4	1.3	1.5	0.6	0.6	1.0	1.0	0.39
2	8.8	5.6	8.4	6.7	6.1	8.4	9.6	7.9	8.5	9.4	9.6	1.05
3	13.4	12.0	13.1	11.6	10.0	12.8	12.3	13.0	13.5	10.7	11.3	0.63
4	12.4	11.4	13.2	12.7	12.2	9.4	9.1	11.6	11.7	8.6	8.2	0.44
5	16.1	14.9	16.4	16.3	16.0	12.9	12.5	11.3	10.7	12.2	12.6	0.57
6	19.6	20.1	19.7	20.2	18.4	16.5	15.7	14.1	14.3	16.3	15.2	0.59
7 (apex)	34.3	34.0	32.9	33.1	30.5	27.1	27.9	26.5	25.1	26.9	27.6	0.97
Total length (cm)	105.3	98.1	104.5	101.2	93.6	88.4	88.6	85.0	84.4	85.1	85.5	2.43
Lodging (0-9)	2.4	2.3	3.0	1.3	1.9	0.3	0.5	0	0	0	0	0.36



leading to a possible build up of precursors and a consequent flush of its biosynthesis as the growth regulator is degraded. The effect of this would be to exaggerate any extension growth occurring at the time. Where LI 700 had been added as the adjuvant, this appeared to coincide with the phase of elongation of the lower stem internodes. It did not occur where Agral had been added as the adjuvant.

While there were no differences in stem length as a result of the type of adjuvant added to chlormequat when applied at GS 32, in both seasons, the addition of LI 700 to chlormequat produced significant increases in grain yield, compared with the addition of Agral. This, however, only occurred in conditions of high fertility, and then the mechanism of this response differed in consecutive seasons.

It appears that the combination of chlormequat and LI 700 increased the growth potential of the crop. The subsequent realization of the increased potential, and, indeed, the mechanism by which it was achieved, was dependent upon other limiting factors, in this case, availability of N and the pattern of crop growth at the time of application. Use of the growth regulator chlormequat in cereals has produced numerous reports of secondary effects,<sup>3</sup> although they are highly variable. These include increased shoot production and survival, increased grain number, reduced grain weight, increased light penetration, and increased longevity of green area. From the data available, it is possible only to speculate that the increased cuticular penetration of chlormequat through the use of LI 700, and its greater persistence within the crop, influenced one or more of the above characteristics in such a way as to increase the potential grain yield. The lack of any differential stem shortening response to chlormequat at GS 32 suggests that there is a limit to the degree of shortening that can be achieved in any one internode. While LI 700 may promote a greater uptake of the growth retardant, the amount taken up in the presence of Agral is sufficient to achieve maximum reduction. It is only in terms of the secondary effects, or from earlier applications, that the differences in uptake and persistence become apparent.

In conclusion, it appears that the nature of the adjuvant can significantly influence the uptake of the growth regulator chlormequat. While both adjuvants increased its uptake and persistence, the effect was significantly greater with LI 700 compared with Agral. On a purely practical basis, this provides a means of extending the effective application period during which chlormequat can be applied to oats. It also promoted additional responses which were shown to significantly increase the yield potential of the crop. The exact mechanism of these responses requires further research.

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## Chapter 60

**ECOLOGICAL ASPECTS OF THE BIOCIDES  
EMULSIFIERS: EMULSOGEN® ITN AND EMULSOGEN® ITL**

A. Neufahrt and Z. Damó

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## ABSTRACT

The adsorption isotherms for standard soil contaminated with moderate and large amounts of organic matter are largely identical. The adsorption of surface-active substances by soil contaminated by large quantities of organic matter is significantly higher than adsorption by moderately contaminated standard soil or quartz sand.

After 16 d of incubation of Emulsogen® ITN and Emulsogen® ITL with biologically reactivated standard soils, degradation rates of 90% were measured. In the screening test, i.e., under sewer outfall conditions, more than 90% of the anionic components and the nonionic surfactant content were removed from the mineral nutrient solution. Under the conditions of the confirmatory test (activated sludge plant), the anionic surfactants were eliminated immediately and 80% of the nonionic content after an adaptation phase of 10 d.

## I. INTRODUCTION

Pesticides are used in formulations which, apart from the active ingredient, contain organic solvents or carriers and surfactants.

As can be seen from the relevant literature and particularly from the studies conducted by Jansen et al.,<sup>9</sup> investigations have been carried out in recent years to determine surfactant-specific effects on the penetration of the active ingredient (a.i.) into plants, and also with a view to improving the activity of the active ingredient. According to the results obtained by Foy and Smith,<sup>5</sup> the effects of surfactants in pesticide formulations are restricted mainly to relatively pronounced stimulation of the penetration of the relevant a.i. into the target organism. As Behrens<sup>1</sup> demonstrated, optimal effects can only be obtained if the a.i. in question is present in the optimal concentration for the target organism.

The fact that surfactants are not only capable of entering into complex chemical reactions with clay minerals, but also, as Weiss<sup>16</sup> demonstrated, are deposited in phyllosilicates by means of ion exchange reactions shows that the use of surfactants in pesticide formulations is not without its problems from an ecological standpoint. When they take place, these processes can affect physicochemical properties such as pH value, ion exchange capacity, and events that occur during the seepage of water. This means that as a result of these physicochemical changes, there may be far-reaching alterations within the types of bacteria and the species of protozoa and metazoa.

We shall therefore attempt to clarify below some important questions, including:

1. Adsorption of the surfactant components onto soils
2. Biodegradability of the pesticide emulsifiers in the soil
3. Biodegradability of the emulsifiers in outfall sewers
4. Biological elimination of these surfactant components in the activated sludge plant

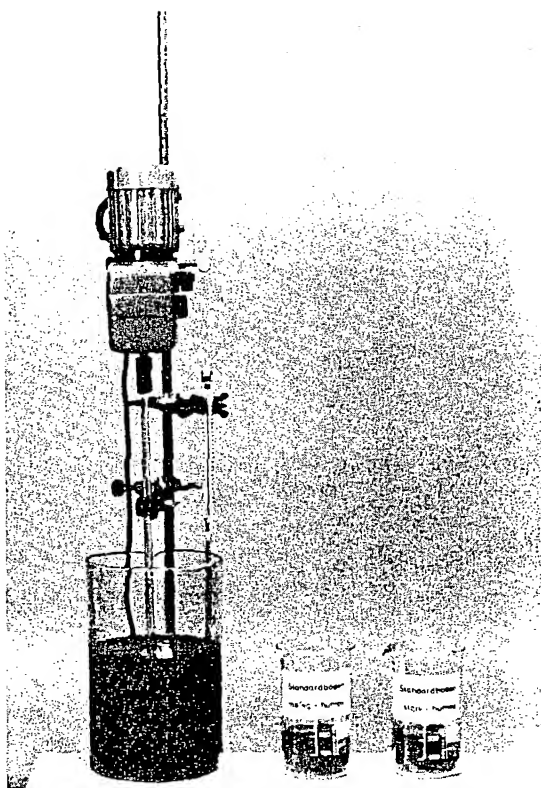
## II. MATERIAL AND METHODS

### A. PESTICIDE EMULSIFIERS

Emulsogen ITN and Emulsogen ITL are multicomponent systems containing various anionic and nonionic surfactants.

### B. PRODUCTION OF ADSORPTION ISOTHERMS

One hundred grams of both a moderately and a highly humous standard soil (Data Sheet No. 37, March 1978, of the Federal Biological Institute for Agriculture and Forestry) were stirred into 2 l of emulsifier solution, as shown in Figure 1.



Equipment used for establishing adsorption isotherms of the pesticide emulsifiers Emulsogen ITN / ITL

FIGURE 1.

Various concentrations of the surfactants ITN and ITL were used. After intensive mixing (stirring) of the suspension for 2 h, the mixture was allowed to stand for 4 h. It was then stirred vigorously for 24 h until adsorption equilibrium was established. After allowing the soil to settle again for 2 h, the supernatant was removed and centrifuged at 4000 rpm.

Surfactant content was determined by the analytical methods specified in the Regulations Governing the Degradability of Anionic and Nonionic Surfactants in Detergents and Cleaners of 30.01.1977 (*Federal Law Gazette I*, p. 244).

### C. SEEPAGE TRIALS

As described by Fink et al.,<sup>4</sup> three chromatographic tubes ( $\emptyset$ , 2.5 cm; length, 15 cm) were filled with 20 g of substrate. The substrates used were

1. Quartz sand (0.1–0.3 mm)
2. Standard soil, moderately humous
3. Standard soil, highly humous

The apparatus is shown in Figure 2.



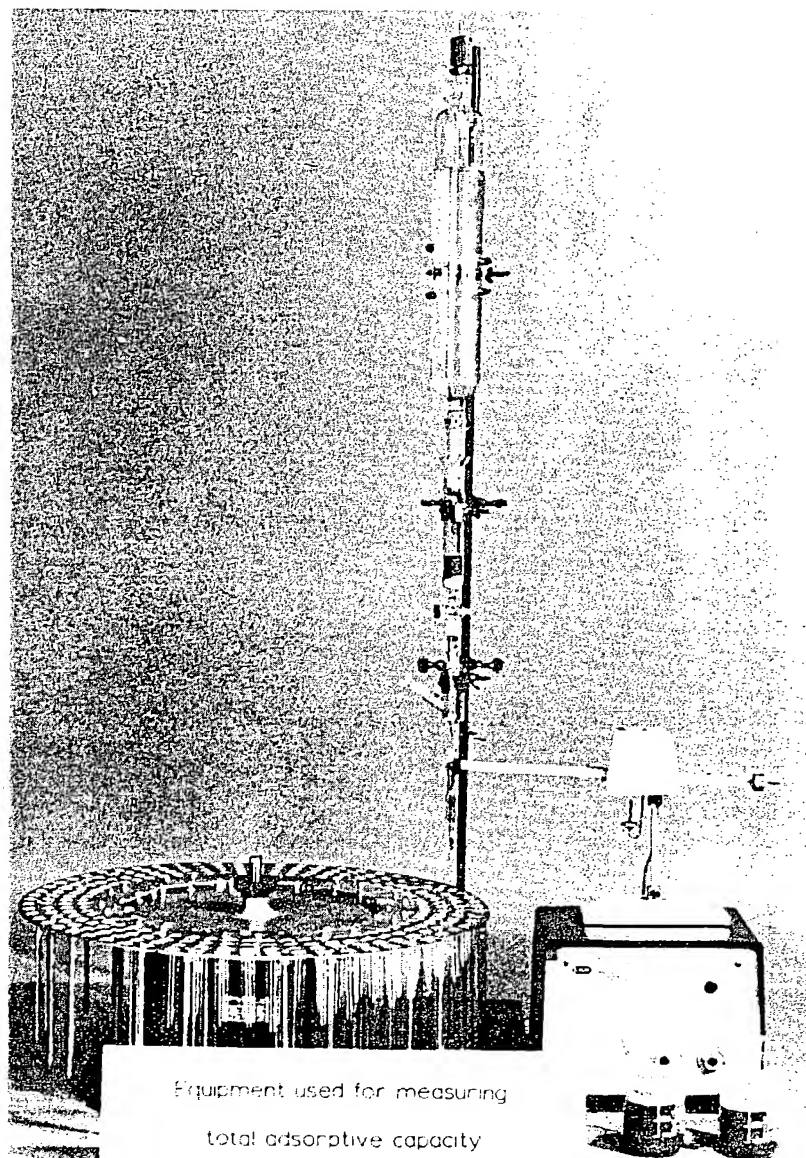


FIGURE 2.

After mounting a glass fiber filter on each tube, the substrates were converted into a "saturated state" by adding distilled water dropwise. After exchanging the glass fiber filter for a round filter of the same type soaked with emulsifier solution, the test solutions (100 ppm ITN and ITL) were added at a rate of five drops per min. In each case, the escaping liquid was fractionated into 10-ml samples using an LKP 3402 B or LKP-7000 fraction collector. The surfactant concentrations were determined by the methods referred to in Section II.B.

#### D. DETERMINATION OF THE BREAKDOWN IN THE SOIL

One kilogram each of sand, and moderately and highly humous standard soil were biologically reactivated by the Weinmann and Schinkel<sup>15</sup> method, and then poured into 300-

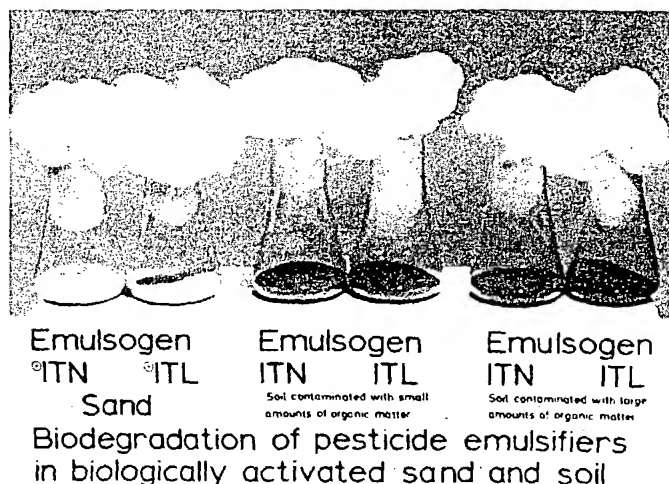


FIGURE 3.

ml Erlenmeyer flasks in aliquots of 100 g. The sand and soils were vigorously mixed with 5 ml of each of the emulsifier solutions to be tested, which contained 30 mg of a.i. (Figure 3).

The vessels were closed with a wad of cotton wool and left in the dark at  $22 \pm 2^\circ\text{C}$  for the duration of the test. Any loss of water that occurred was made up. The sand and soil were dried after 0, 8, 16, 32, and 42 d of incubation. The surfactants were extracted first with an ethanol/toluene and then with an acetone/methylene chloride mixture. The solvents were distilled off, the residue dissolved in distilled water, and the concentrations of anionic and nonionic surfactants determined.

Possible toxic effects of the emulsifier concentration on the soil bacteria were monitored using the method of TTC-dehydrogenase activity determination developed by Klapwijk et al.<sup>10</sup>

#### E. BIODEGRADATION OF EMULSOGEN ITN AND ITL IN THE SELECTION TEST AND CONFIRMATORY TEST

The studies of the biological degradation of the multicomponent systems Emulsogen ITN and Emulsogen ITL were carried out in accordance with the directives for the implementation of the German Detergents Law (see Section II.B).

### III. RESULTS AND DISCUSSION

For a better understanding of possible inhibitory effects, particularly on the microflora and fauna of the soil, caused by the pesticide emulsifiers Emulsogen ITN and ITL, it is important first to gain an insight into the specific adsorption capacities of the two test soils.

The results of these studies are summarized in Figure 4. The abscissa shows the difference in concentration,  $C_0 - C$ , after establishment of equilibrium. The amount of surfactant adsorbed in milligrams per gram of soil is plotted on the ordinate.

As the adsorption isotherms for both emulsifiers show, with an initial concentration  $C_0 = 20,000$  ppm, 5 mg of anionic surfactant components and 6 mg of nonionic surfactant components per gram of moderately humous soil were measured for Emulsogen ITN, and 9 mg of anionic surfactant components and 10 mg of nonionic surfactant components per gram of moderately humous soil in an identical test with Emulsogen ITL.

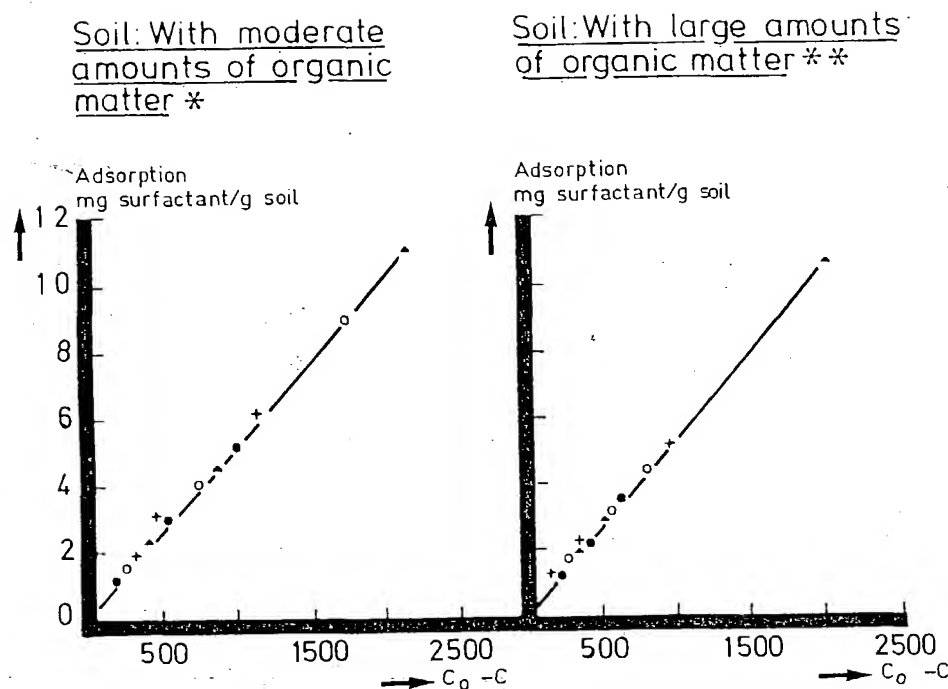


FIGURE 4. Adsorption isotherms of the anionic and nonionic components of the emulsifiers Emulsogen ITN and Emulsogen ITL. ●, anionic surfactants; ○, anionic; +, nonionic; ▲, nonionic.

With  $C_0 = 20,000$  ppm, in the highly humous soil, 3 mg of the anionic components and 5 mg of the nonionic components of Emulsogen ITN were adsorbed per gram of soil. The corresponding values for Emulsogen ITL were 4 mg of anionic and 10 mg of nonionic surfactants per gram of soil.

Additional studies of the adsorption behavior of the anionic and nonionic surfactant components of Emulsogen ITN and ITL in the seepage test (Figure 5) show that both the standard soils (moderately and highly humous), as well as the sand used, adsorb nonionic components to a greater extent than they do anionic components. Figure 6 shows typical curves for the components of Emulsogen ITN and ITL for the highly humous standard soil. In this graph, the area above the curves (up to the maximum concentration  $C/C_0 = 1$ ) is directly proportional to the amounts of surfactant adsorbed.

The biological breakdown, in reactivated sand and in the reactivated standard soils, of the surface-active compounds of the pesticide emulsifiers tested is shown in Figure 7. This graph shows that 90% of the surfactant components are eliminated by the bacteria in the soil after just 16 d of incubation. In sand, which is difficult to reactivate biologically, elimination rates of 8 and 3%, were measured for ITN and ITL, respectively, over the same period.

The TTC dehydrogenase enzyme activity of the biologically reactivated sand was as little as  $10^{-5}$  that of the TTC-dehydrogenase activity of the standard soils used. A toxic effect of the pesticide emulsifiers tested on the bacteria in the soil can be ruled out on the basis of these measured values. This is important because, as was demonstrated by Hartmann,<sup>8</sup> soil bacteria are more sensitive to surfactants than are wastewater bacteria.

The soil bacteria, which are mainly Gram-positive, are inhibited by surfactants, particularly anionic surfactants, to a much greater extent than wastewater bacteria, which are predominantly Gram-negative.

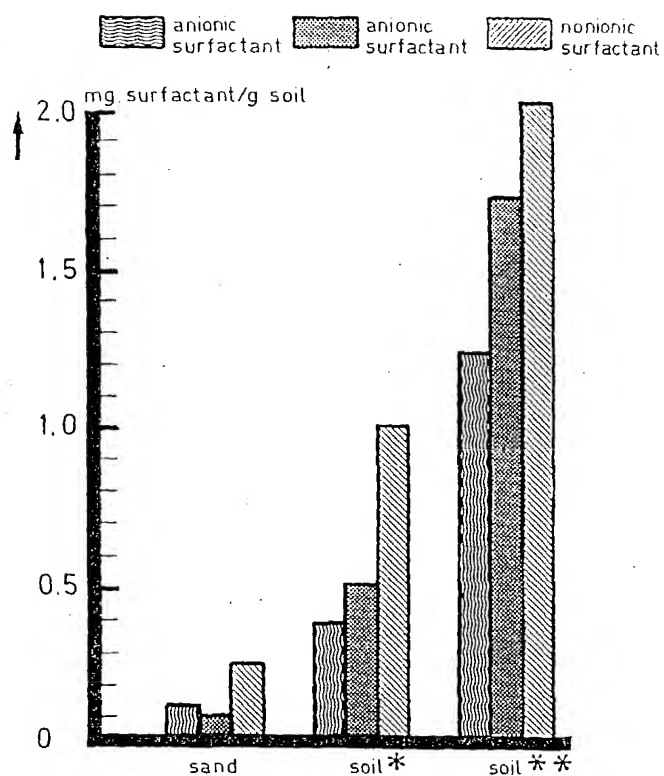


FIGURE 5. Leaching experiments with sand and soils.

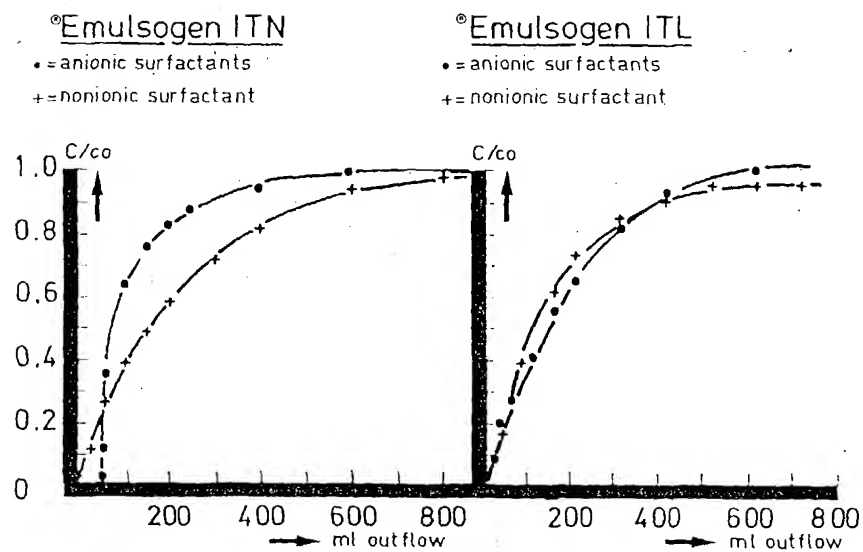


FIGURE 6. Total adsorption of Emulsogen ITN and Emulsogen ITL by soil contaminated with large amounts of organic matter.



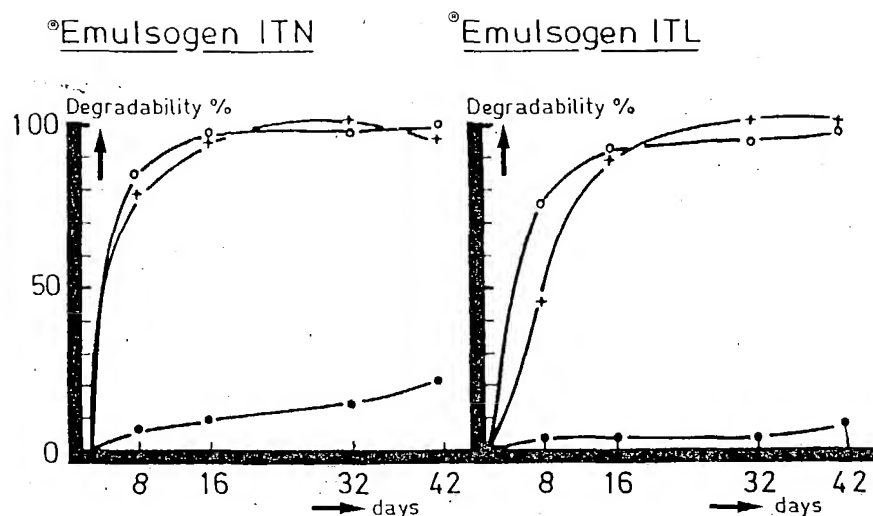


FIGURE 7. Biodegradability of the ag-emulsifiers in sand and soils. ●, sand; ○, soil\*; +, soil\*\*.

It was demonstrated by means of a leaching test, in which  $^3\text{H}$ -labeled emulsifier material was used, that even with a rainfall of 250 mm, it still takes 150 d to penetrate to a depth of 40 cm. This low seepage rate, together with the good biodegradability in the soil, rules out the possibility of contamination of groundwater by either of the emulsifier systems (Figure 7).

As is also apparent from the results of breakdown trials in outfall sewers (selection test) shown in Figure 8, both pesticide emulsifiers can be classified as "biologically soft" compounds. More than 80% of the surfactants used (total carbon concentration of 5 ppm) are broken down after only 6 d.

These good breakdown results mean that there is no risk to the biotopes' streams, rivers, and lakes. Even if relatively high concentrated solutions are inadvertently discharged into the communal wastewater treatment plant via the sewage system, there is no risk of temporary impairment of the degradability of the activated sludge plant.

As can be seen from Figure 9, high elimination rates can be achieved in laboratory-activated sludge plants (confirmatory test) with a dwell time of 3 h. As the curves show, the anionic components of nonadapted activated sludge are immediately broken down to a high degree. Optimum breakdown values for the nonionic components are obtained only after a 10-d period of adaptation of the activated sludge to the relevant compounds.

In summary, when used correctly, the good biologically eliminability of the two pesticide emulsifiers ITN and ITL rules out the possibility of irreversible impairment of the biotopes' soil and running water, and of communal wastewater treatment plants. These results have been confirmed by recent work, e.g., the status seminar on alkylbenzene sulfonates (LAS) held at Aachen in 1988.<sup>2,3,6,7,11-14</sup>



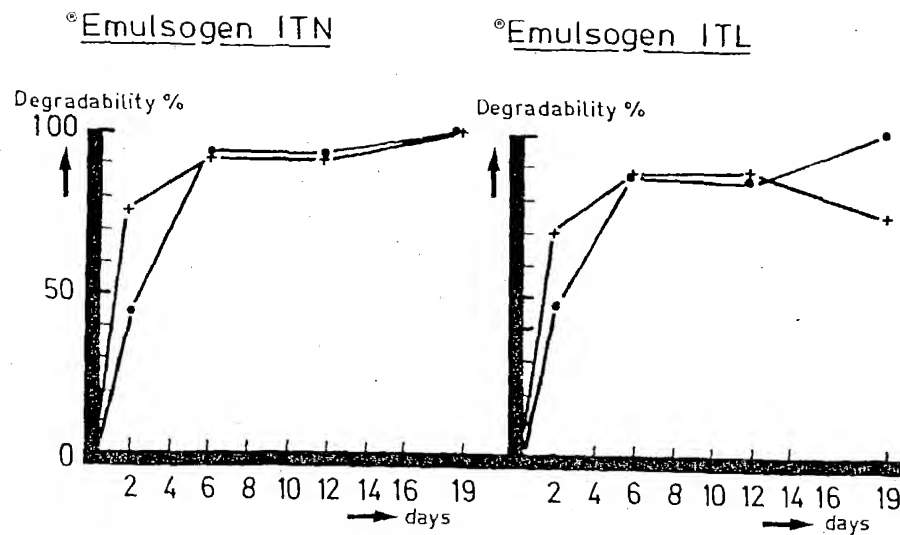


FIGURE 8. Biodegradability of Emulsogen ITN/ITL according to the OECD screening test. ●, anionic surfactants; +, nonionic surfactants.

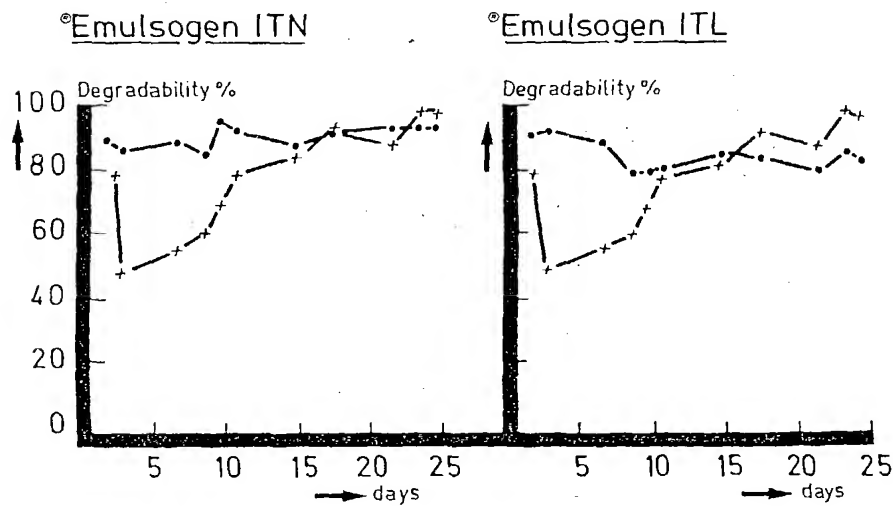


FIGURE 9. Biodegradability of Emulsogen ITN and ITL according to the OECD confirmatory test. ●, anionic surfactants; +, nonionic surfactants.

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## Chapter 61

INFLUENCE OF SURFACTANT-OIL COMBINATIONS ON THE  
ACTIVITY OF FOLIAR-APPLIED FUNGICIDESWalter Steurbaut, H. S. Megahed, G. Van Roey, T. Melkebeke, and  
W. Dejonckheere

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## ABSTRACT

In addition to their influence on the physicochemical properties and spray performance of formulations, the presence of adjuvants in the spray liquid can also influence the phytotoxic properties of the spray solution. The chemical composition of the surfactant plays a particularly important role. Fungitoxicity is influenced, as measured on three different fungi *in vitro*, but the interactions between active ingredient, adjuvant, and fungi are very specific. Possible relationships between biological activity and physicochemical properties are discussed.

## I. INTRODUCTION

In the first part of this study,<sup>21</sup> the influence of adjuvants on the physicochemical properties of a fungicide spray solution and the changes of the spray performance are studied. This is especially important for contact pesticides, which have to form a continuous protective layer on the leaf surface to obtain maximum protection. Systemic compounds, however, must overcome some extra barriers before they come into contact with the target. They have to penetrate into the plant, followed by a transport process to the infection site.

These factors are influenced not only by the lipophilic-hydrophilic properties of the active ingredient itself,<sup>17</sup> but also by the formulation type<sup>13,19</sup> and the formulation ingredients.<sup>8,12</sup> Hence, one questions whether there is any way to improve systemic fungicide performance by the addition of suitable adjuvants to the spray solution. Because adjuvants are already associated with better wetting and spreading properties, this study investigated the influence of some adjuvants on the penetration of the active ingredient in the leaf, the possible phytotoxic side effects, and the final fungitoxicity.

## II. MATERIALS AND METHODS

### A. MATERIALS

The same formulations and adjuvants in the first part of this study<sup>21</sup> have been used.

### B. MEASUREMENT OF THE PENETRATION OF THE ACTIVE INGREDIENT INTO THE LEAVES

Wheat (*Triticum aestivum* L.) seeds (var. Aveve 905) were sown in plastic pots filled with an organic soil. The plants were kept for 3 weeks in the greenhouse until three full leaves were present. The aerial part was cut off just above the soil level and put with its basal part into a water reservoir (test tube) to prevent wilting.

A strip of polyurethane (open-cell type, 80 pores per inch; Recticel Belgium) with a cross section of exactly  $1 \times 1$  cm was put on both sides of the basal part of the second leaf. The sides were held together at the ends with paper clips and impregnated with 2 ml of the spray solution containing the formulation (normal field rate) with or without adjuvants (0.1% for surfactant and 0.3% for surfactant + oil). After 24 h, the upper part of the leaf was cut off at a distance of 0.5 cm from the strips and the active ingredient analyzed by a suitable analytical method. Prochloraz residues were extracted according to the method described by Dejonckheere et al.<sup>9</sup> and analyzed by gas liquid chromatography (GLC) with an electron capture detector under the conditions described in Table 1.

For oxadixyl residue determination, the sample was homogenized with 200 ml of extraction solvent (petroleum-ether/acetone, 1:1), filtered over a Buchner filter, and rinsed with a 50-ml extraction solution. The combined filtrates were shaken for 2 min together with 200 ml of distilled water and a 25-ml saturated sodium chloride solution in a separating

TABLE I  
GLC Conditions for Residue Analyses

Instrument type	Prochloraz	Oxadixyl	Flutriafof
Column packing material	5% OV210 + 2% OV17 on Gaschrom Q (80-100)	5% OV210 + 2% OV17 on Gaschrom Q (80-100)	5% OV210 + 2% OV17 on Gaschrom Q (80-100)
Length	0.5 m	0.5 m	0.5 m
Internal diameter	2 mm	2 mm	2 mm
Operating conditions			
Oven temp.	240°C	240°C	215°C
Injector temp.	250°C	250°C	230°C
Detector temp.	300°C	250°C	250°C
Carrier gas	N <sub>2</sub>	N <sub>2</sub>	N <sub>2</sub>
Flow rate	40 ml/min	35 ml/min	40 ml/min
Detector	EC	TSD	TSD
Retention time	7.0 min	2.0 min	2.2 min
Detection limit (ppm)	0.05	0.02	0.05
Recovery	90%	95%	>90%

funnel (500 ml). After separation of the layers, the water layer was collected and the organic layer extracted again with water and a sodium chloride solution. The combined aqueous layers were measured, and half of the volume was extracted twice with 10 ml of dichloromethane, which was dried over anhydrous sodium sulfate in an Allihn tube. After rinsing the tube, the combined dichloromethane fractions were evaporated under vacuum and the residue dissolved in 25 ml of acetone. This solution was evaporated again to eliminate all dichloromethane. The residue was finally dissolved in 5 ml of acetone for GLC analysis with the conditions mentioned in Table 1.

Flutriafof residues were extracted by homogenizing the sample with 200 ml of acetone. After filtering over a Buchner filter and rinsing with 50 ml of acetone, the volume of the filtrate was measured. Half of the filtrate was evaporated under a vacuum until an aqueous residue remained at 40°C. Distilled water (150 ml) and 25 ml of sodium chloride solution were added with the extract in a separating funnel. After extraction twice with 100 ml of dichloromethane, the organic layers were dried over anhydrous sodium sulfate in an Allihn tube. After rinsing the tube with 25 ml of dichloromethane, the collected organic phases were evaporated under vacuum, the last milliliter under an air stream. Acetone (25 ml) was added to the dry residue and again evaporated in order to eliminate all dichloromethane. Finally the residue was dissolved in 5 ml of acetone for GLC analysis, as described in Table 1.

## C. DETERMINATION OF PHYTOTOXICITY

### 1. Influence on Germination

Ten intact wheat seeds (Aveve 905) were put in a petri dish (9 cm i.d.) on a layer of ten filter papers (Schleicher & Schuell no 595) and moistened with 10 ml of a solution containing formulation and/or adjuvants. Water was used as a control. The dishes were put in the dark at room temperature and germination was determined after 1 week as the percentage of the control. The results are the average of a triplicate treatment.

### 2. Influence on Growth, Respiration, and Nutrient Uptake

Cucumber seeds (*Cucumis sativus* L. var. Marketer) were germinated on a moistened vermiculite substrate, and after 1 week the seedlings were transferred to a perforated card in such a way that the roots were hanging in a hydroponic nutrient solution with or without



additional formulation and/or adjuvants.<sup>20</sup> After 2 weeks, the average weight of five plants was measured. The roots were cut off and weighed. The amount of nutrient solution taken up by five plants during the test period was taken as a measure of the transpiration rate. The ammonium and nitrate uptake was measured by determining the difference between their amount present in the nutrient solution at the beginning and end of the exposure period according to standard methods.<sup>2</sup>

#### D. DETERMINATION OF THE FUNGITOXICITY IN VITRO

Fungitoxicity was determined for *Fusarium sambucinum* Fuckel CBS 184.31, *Pythium debaryanum* Hesse CBS 26030, and *Botrytis cinerea* pers. ex. Fr. (Laboratory of Plant Pathology, State University, Gent). The first two fungi were grown on a potato dextrose agar (PDA, 39 g/l at 25°C), and the latter on malt extract agar (MEA, 48 g/l at 25°C). Stock solutions of formulations and/or adjuvants were made in sterile distilled water, except for prochloraz, where methanol was used. Further dilutions were all made with water in such a way that 0.5 ml was added to 50 ml of cooled (45°C) agar medium to obtain the desired concentrations. Three petri dishes (9 cm i.d.) were filled with 12 ml of this medium, and after cooling to room temperature, they were inoculated with a disc (6 mm diameter) of fungal mycelium taken at the edge of an active colony. After incubation at 25°C, the average radical growth was measured after 5 d for *Fusarium* and 3 d for *Botrytis* and *Pythium*. The percentage of inhibition was calculated according to Cohen et al.:<sup>7</sup>

$$\% \text{ inhibition} = 100 - (R^2/r^2 \times 100)$$

where R is the radius for treated medium and r, the radius for untreated medium.

### III. RESULTS AND DISCUSSION

#### A. INFLUENCE OF ADJUVANTS ON THE PENETRATION OF THE ACTIVE INGREDIENT IN THE LEAF

It has already been demonstrated by several authors<sup>1,3,22,27</sup> that surfactants can enhance the uptake of pesticides by plants. Different experimental procedures were followed in these investigations ranging from uptake of labeled compounds<sup>6,11,18</sup> to residue analysis of the amount of penetrated active ingredient (a.i.).<sup>15,20</sup> A problem for all these studies is that it is difficult to separate the factors which are involved in the total process of application, which consists of a complex and interactive system of spreading, penetration, and transport.

The intention of this study was to overcome these interactions with special methodology. By replacing droplet application by an impregnated polyurethane plug with constant contact area on the leaf surface, the effect of different spreading behaviors of droplets is avoided so that only penetration is involved. The results in Table 2 show the relative percentage of the uptake compared with the application of the spray solution without adjuvants.

Almost all adjuvants result in enhanced uptake of the a.i. The POE-hexitan ester (Atplus® 201) and the POE-nonylphenol (Renex® 697), however, had only a minor influence, while especially the POE-alcohol (Atplus 230) and the organosilicone surfactant (Tegopren® 5878) had a very pronounced influence on uptake. The behavior was also different among the oil adjuvants. Atplus 411F, 412, and 420 had only a negligible impact, while Atplus 417 and 419 showed excellent penetration enhancement.

It is worth mentioning that the values in Table 2 are relative to the spray solution of the formulation without surfactant. Although these values demonstrate that the uptake for wettable powder (WP) formulations was more enhanced by adjuvants than for EC and suspension concentrate, (SC), the absolute values indicate that enhancement of the uptake for the latter

TABLE 2  
Penetration in Leaves as Percent of Treatment  
Without Surfactants

Surfactant	Flutriafol	Prochloraz	Oxadixyl	Average X
None	100	100	100	100
Atplus 201	119	96	113	109
Atplus 230	142	135	<u>260</u>	<u>179</u>
Atplus 204	96	<u>173</u>	<u>162</u>	144
Atplus 203	138	130	<u>177</u>	148
Atplus 284	118	<u>156</u>	<u>151</u>	142
Tegopren 5878	<u>215</u>	<u>305</u>	<u>430</u>	<u>317</u>
Renex 697	99	112	104	105
Atplus411F	111	101	93	102
Atplus412	97	121	112	110
Atplus 415	146	136	146	143
Atplus 417	<u>168</u>	<u>152</u>	<u>233</u>	<u>184</u>
Atplus 419	<u>172</u>	<u>163</u>	<u>225</u>	<u>187</u>
Atplus 420	93	116	143	117
Average X	132	146	181	153

Note: Boldface numbers + 25% compared with "no surfactant".

Boldface numbers + 50% compared with "no surfactant".

formulation types was also very high, since 100% relative uptake for flutriafol, prochloraz, and oxadixyl is equivalent to 1.1, 0.6, and 0.7 ppm, respectively, in the upper part of the leaf. It is obvious that the smaller relative uptake increase for flutriafol (SC) was, in absolute terms, sometimes higher than that for oxadixyl (WP) because the initial uptake was higher for SC formulations due to the presence of higher surfactant levels. This can explain why the addition of surfactants and oils as adjuvants results in a more pronounced relative effect for WP formulations.

There seems to be no direct relationship between penetration in the leaves and the physicochemical parameters which play an important role in spreading (contact angle, surface tension). This may explain why there is no direct relationship between the spreading and penetrant properties of a spray solution. Some adjuvants are bad spreaders but good penetrants (e.g., Atplus 284), while others are good spreaders but bad penetrants (e.g., Renex 697). Only Atplus 230 and certainly Tegopren 5878 combined both effects in a favorable way for all formulations.

#### B. INFLUENCE OF ADJUVANTS ON THE PHYTOTOXICITY OF FUNGICIDE SPRAY APPLICATIONS

Fungicides, especially systemic fungicides, can have phytotoxic side effects because their mode of action on fungi can interfere with some biochemical processes of higher plants. Adjuvants can enhance the uptake and transport of systemic fungicides in the plant, leading to an accumulation of the a.i. and thereby to a higher risk of phytotoxicity.

Table 3 contains a survey of the phytotoxicity tests for flutriafol (SC), prochloraz (EC), and oxadixyl (WP). Taking into account the described experimental circumstances and concentrations, one may conclude that the formulations had an intrinsic phytotoxicity that was higher for flutriafol (75% growth of control) than for prochloraz (85%) and oxadixyl (87%). The addition of adjuvants resulted in an increased phytotoxicity of prochloraz, for both surfactant and oil adjuvants. Flutriafol toxicity was only influenced by oils, while oxadixyl toxicity was not increased in a significant way.

TABLE 3  
Phytotoxicity (% Growth of Control) of  
Surfactant-Fungicide Combinations

Surfactant ( $\frac{1}{5}$ of fungicide conc)	Flutriafol (20 ppm)	Prochloraz (30 ppm)	Oxadixyl (100 ppm)
None	75	85	87
Atplus 201	69	72	77
Atplus 230	73	67	88
Atplus 204	67	49	88
Atplus 203	61	65	82
Atplus 284	78	80	80
Tegopren 5878	81	82	90
Renex 697	61	56	82
Atplus 411F	65	51	90
Atplus 412	68	80	90
Atplus 415	51	89	82
Atplus 417	48	68	73
Atplus 419	73	80	73
Atplus 420	53	50	89

Note: Boldface numbers 20% higher phytotoxicity compared with "no surfactant".

Figure 1 shows the relationship between the phytotoxicity of spray solutions as a function of adjuvant concentration. The different behavior of prochloraz and flutriafol when surfactants were added, compared with oxadixyl is remarkable.

The presence of solvents and higher surfactant concentration in the formulation probably was influenced more by the extra phytotoxic input of the adjuvant. Furthermore, the phytotoxicity of Atplus 203 was more pronounced at increasing levels than was that of Tegopren 5787. The changing influence of surfactant concentrations makes the predictability of phytotoxic side effects of adjuvants more complicated and dependent on a complex system of interactions between plant, formulation types, a.i., adjuvant type, and adjuvant concentration.

The choice of measuring parameters can also be critical for the estimation of phytotoxicity. Table 4 contains a survey of the evaluation of phytotoxicity on cucumber (*Cucumis sativus* C.) plants in a hydroculture system treated with 5 ppm of fungicide alone or in combination with 5 ppm of Atplus 201. Phytotoxicity was established with five different experimental determinations on five plants after two weeks: weight increase, weight of the root system, amount of nutrient solution taken up, and nitrate and ammonium uptake. The results were classified into four categories: (A) more than 75% of the control, (B) between 75 and 50%, (C) between 50 and 25%, and (D) less than 25%.

These results indicate that phytotoxicity is very difficult to evaluate with only one parameter. It is striking that the parameters can be very different among themselves. Prochloraz and metalaxyl had no important differences. Imazalil only influenced growth inhibition, but this was not reflected by the other parameters. Flutriafol and propamocarb had more pronounced phytotoxic effects. The addition of Atplus 201, which by itself had only minor phytotoxic effects, generally gave rise to an increase in phytotoxicity, but this influence was highly variable and not specific to a particular parameter. The addition of Atplus 201 was more toxic in combination with EC formulations than with WP formulations. This seems to confirm the supposition that formulation constituents such as solvents and surfactants can be as important for phytotoxic side effects as the a.i. itself.<sup>14,26</sup>

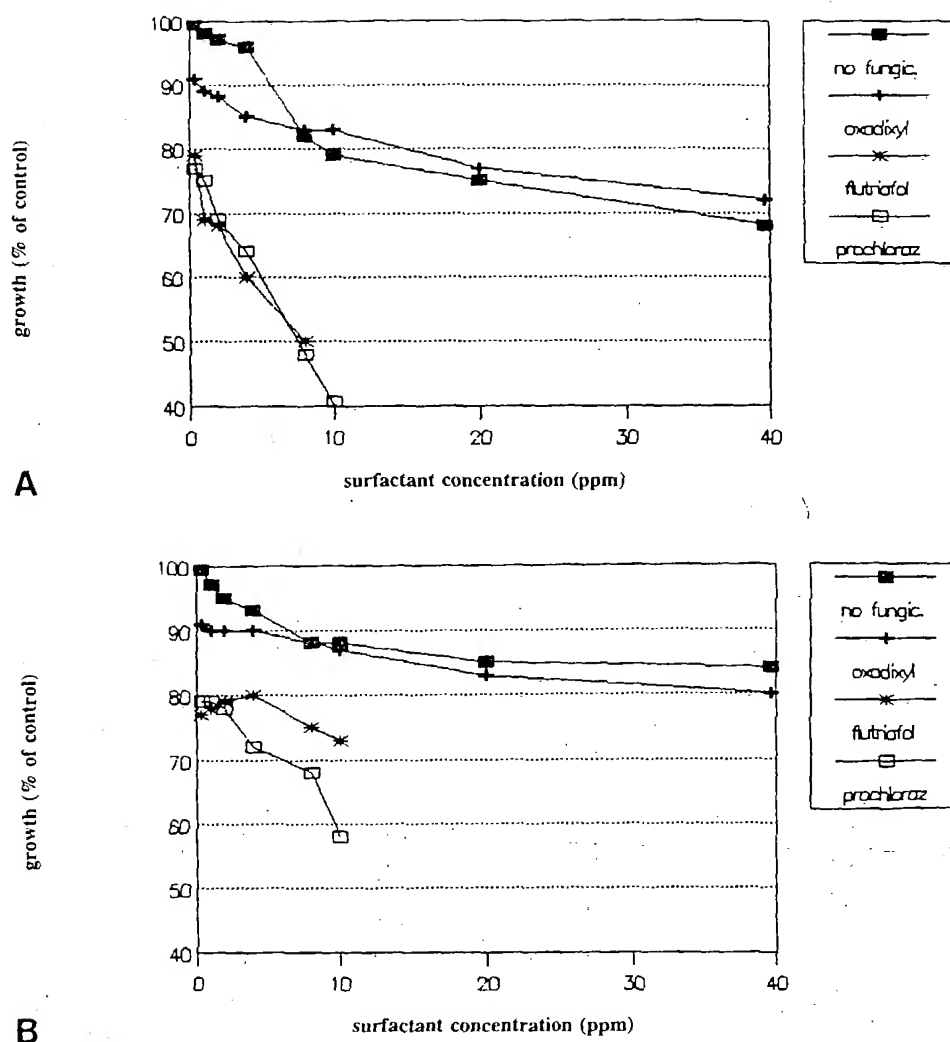


FIGURE 1. Influence of adjuvant concentration on the phytotoxicity of spray solution (containing 100 ppm oxadixyl, 20 ppm flutriafol, and 30 ppm prochloraz). (A) Atplus 203; (B) Tegopren 5878.

TABLE 4  
Phytotoxicity According to Different Experimental  
Parameters (See Text)

Fungicide	Without surfactant	With surfactant
None	AAAAA	AAAAB
Flutriafol (SC)	DDBAA	DDCAC
Prochloraz (EC)	AABAA	BBBAC
Imazalil (EC)	DBBBB	DCBCB
Propamocarb (SC)	CBABB	CDABC
Metalaxyl (WP)	ABBAA	ABCAA

TABLE 5  
Calculated Parameters for Uptake

Surfactant	F <sup>2</sup> × % penetration			I.D. × % penetration		
	Flutriafol	Prochloraz	Oxadixyl	Flutriafol	Prochloraz	Oxadixyl
None	313	303	219	203	211	378
Atplus 201	352	291	234	<b>245</b>	191	329
Atplus 230	<b>620</b>	<b>578</b>	<b>1270</b>	204	201	260
Atplus 204	384	<b>599</b>	<b>519</b>	149	<b>294</b>	296
Atplus 203	<b>574</b>	<b>504</b>	<b>634</b>	210	205	264
Atplus 284	357	<b>494</b>	<b>315</b>	<b>234</b>	<b>293</b>	<b>415</b>
Tegopren 5878	<b>2026</b>	<b>2875</b>	<b>4053</b>	133	189	267
Renex 697	321	<b>435</b>	315	178	177	205
Atplus 411F	321	240	206	233	196	257
Atplus 412	287	<b>392</b>	<b>280</b>	190	219	277
Atplus 415	<b>463</b>	<b>460</b>	<b>389</b>	<b>274</b>	238	323
Atplus 417	<b>532</b>	<b>412</b>	<b>604</b>	<b>319</b>	<b>275</b>	<b>545</b>
Atplus 419	<b>570</b>	<b>698</b>	<b>847</b>	<b>304</b>	241	367
Atplus 420	288	268	322	183	219	382

Note: Boldface numbers + 25% compared with "no surfactant". Boldface numbers + .50% compared with "no surfactant". I.D., initial deposit.

### C. ESTIMATION OF PHYTOTOXICITY WITH SPREADING AND UPTAKE PARAMETERS

From a theoretical point of view, phytotoxicity caused by spray application of systemic fungicides is the result of three different but co-acting factors. First, leaf coverage is involved, resulting in a greater spray contact area with the surface. Second, the penetrating ability of the a.i. is influenced by the presence of formulation constituents or adjuvants. And third, the phytotoxicity of the a.i. and the other spray constituents (solvents, surfactants) can play a role.<sup>23</sup>

For spray applications not exceeding run-off conditions, the spread coefficient (square value) can be considered a good indicator of the contact area.<sup>21</sup> For high-volume applications exceeding the run-off stadium, the calculated maximum initial deposit at run-off can be evaluated as the amount of a.i. present for uptake. Multiplying these coverage parameters with an indicator for uptake, such as the experimentally determined relative penetration of this study, can possibly give a useful indicator of the overall uptake of a.i. after a spray application and, consequently, of the phytotoxicity. These calculated values are given in Table 5.

From these values, it can be concluded that with low-volume applications before run-off (with F<sup>2</sup> as the parameter for initial deposit), the presence of adjuvants in the spray can give an increased uptake for most of the combinations. Only the hexitan ester Atplus 201 and the spray oil Atplus 411F yielded no important improvements. Very good values, however, were obtained with the alcohol Atplus 230, the alcohol containing Atplus 203, the standard oils Atplus 415, 417, and 419, and the outstanding silicone copolymer Tegopren 5878. In some cases, the values of both factors (spreading and penetration) were so conflicting and opposite that they neutralized the advantageous effect of one of them. This is the case for Atplus 284, an amine surfactant with good penetrating properties which were suppressed by bad coverage. The opposite effect was operative for the nonylphenol Renex 697, which is a relatively good spreader but a bad penetrant.

For high-volume spraying beyond run-off conditions, the indicator for good overall uptake is more dependent on the maximum initial deposit (I.D.). Multiplication of this value



TABLE 6  
Fungitoxicity ( $ED_{50}$  in ppm) of Surfactants  
and Fungicides

	<i>Fusarium</i>	<i>Pythium</i>	<i>Botrytis</i>
Surfactant			
Atplus 201	100	800	1200
Atplus 230	50	500	20
Atplus 204	500	800	100
Atplus 203	50	100	50
Atplus 284	1000	800	15
Tegopren 5878	5	2000	50
Atplus 412	500	>2000	200
Atplus 417	100	>2000	5
Atplus 419	800	>2000	75
Fungicide			
Flutriafol	0.8	1000	0.5
Prochloraz	0.1	30	0.3
Oxadixyl	0.2	5	2.0
Metalaxyl	0.5	8	5.0

with the experimental penetration parameter of this study (Table 5) yields values different from those obtained with the spread factor for low-volume applications.

The presence of adjuvants can give rise to lower initial deposits due to the progressive merging and flow down of adjacent drops. The improved spreading by the adjuvant does not condition advantageously the contact area, but, rather, minimizes the initial deposit. Very good spreaders such as the silicone surfactant Tegopren 5878 yielded very low deposit values and, consequently, a loss of total uptake due to a lack of sufficient a.i. on the surface.

These conflicting factors are apparently not present with oil adjuvants, which do not have extreme and opposite influences. Their combined effect results in a synergizing activity. Also remarkable were the good values for the amine Atplus 284, is a good penetrant for herbicides.<sup>4,16,25</sup> Although there is no significant mathematical correlation between this calculated parameter and phytotoxicity, it is still possible to draw some interesting conclusions from these values.

#### D. INFLUENCE OF ADJUVANTS ON THE FUNGITOXICITY OF FUNGICIDE SPRAY SOLUTIONS

Surfactants and oils used as adjuvants can have intrinsic fungitoxic or fungistatic activities.<sup>5,10,24</sup> The results in Table 6 indicate that this activity varies from surfactant to surfactant and is dependent on the fungi. For example, the oil adjuvant Atplus 411F was very active against *Botrytis*, but totally inactive against *Pythium*, while Tegopren 5878 was very active against *Fusarium*, but also inactive against *Pythium*. Generally, *Botrytis* was more sensitive (average  $ED_{50}$  = 190 ppm) than *Fusarium* (350) and *Pythium* (1280). However, compared with fungicides, these average values were high: 0.4, 2, and 36 ppm for *Fusarium*, *Botrytis*, and *Pythium*, respectively.

Combinations of fungicide formulations with adjuvants yielded very confusing and, at first sight illogical results. The interactions between fungi, a.i., adjuvants, and even their respective concentrations were so complex that no general trends could be established. This is illustrated in a series of experiments, the results of which are given in Tables 7, 8, and 9.

Fungitoxicity of surfactants with flutriafol on different fungi (Table 7) generally resulted in an improvement of the activity of the corresponding spray liquid without adjuvant. Taking

TABLE 7  
Fungitoxicity (% Growth Inhibition of Control) of  
Flutriafol-Surfactant Combinations

Surfactant	<i>Fusarium</i> <sup>a</sup>		<i>Pythium</i> <sup>b</sup>		<i>Botrytis</i> <sup>c</sup>	
			Flutriafol			
	0	1 ppm	0	1 ppm	0	1 ppm
None	0	64	0	7	0	77
Atplus 201	35	64 a	18	31 s	23	76 aa
Atplus 230	4	66 aa	12	50 ss	30	80 a
Atplus 204	14	50 aa	6	12 o	20	71 aa
Atplus 203	27	69 a	26	56 s	37	79 a
Atplus 284	20	74 o	7	31 ss	37	79 a
Tegopren 5878	15	82 o	5	16 s	14	73 aa
Atplus 412	18	60 aa	1	12 o	21	76 a
Atplus 417	21	59 aa	20	33 o	71	76 a
Atplus 419	28	73a	2	31 ss	33	79 a

Note: aaa is combined treatment < 1/2 sum separate treatments. aa is combined treatment < highest separate treatment. a is combined treatment < sum separate treatments - 20%. o is combined treatment = sum separate treatments ± 20%. s is combined treatment > sum separate treatments + 20%. ss is combined treatment > 2 × sum separate treatments.

<sup>a</sup> 10 ppm surfactant.

<sup>b</sup> 100 ppm surfactant.

<sup>c</sup> 10 ppm surfactant.

TABLE 8  
Fungitoxicity (% Growth Inhibition of Control) of  
Metalaxyl-Surfactant Combinations

Surfactant	<i>Fusarium</i> <sup>a</sup>		<i>Pythium</i> <sup>b</sup>		<i>Botrytis</i> <sup>c</sup>	
			Metalaxyl			
	0	1 ppm	0	1 ppm	0	1 ppm
None	0	67	0	72	0	64
Atplus 201	35	77 a	18	58 aa	23	59 a
Atplus 230	4	38 aa	12	100 ss	30	76 a
Atplus 204	15	57 aa	6	100 ss	20	61 aa
Atplus 203	27	64 aa	26	59 aa	37	78 a
Atplus 284	20	84 o	7	73 o	37	81 a
Tegopren 5878	15	84 o	5	59 aa	14	62 a
Atplus 412	17	86 o	1	72 o	21	64 a
Atplus 417	21	77 o	20	67 aa	71	61 aa
Atplus 419	28	85 o	2	55 aa	33	74 a

Note: aaa is combined treatment < 1/2 sum separate treatments. aa is combined treatment < highest separate treatment. a is combined treatment < sum separate treatments - 20%. o is combined treatment = sum separate treatments ± 20%. s is combined treatment > sum separate treatments + 20%. ss is combined treatment > 2 × sum separate treatments.

<sup>a</sup> 10 ppm surfactant.

<sup>b</sup> 100 ppm surfactant.

<sup>c</sup> 10 ppm surfactant.

TABLE 9  
Fungitoxicity (*Pythium*) (% Growth Inhibition of Control) of  
Surfactant-Fungicide Combinations

Surfactant (100 ppm)	No fungicide (0 ppm)	Flutriafol (100 ppm)	Prochloraz (30 ppm)	Metalaxyl (10 ppm)	Oxadixyl (10 ppm)
None	0	7	64	73	71
Atplus 201	18	31 s	82 o	58 aa	72 o
Atplus 230	12	50 ss	92 s	100 s	100 s
Atplus 204	6	12 o	35 s	100 s	79 o
Atplus 203	26	56 s	88 o	59 aa	78 s
Atplus 284	7	31 ss	86 o	73 o	100 s
Tegopren 5878	5	16 s	81 o	59 aa	83 o
Atplus 412	1	9 o	61 o	100 s	72 o
Atplus 417	21	32 o	80 o	100 s	66 aa
Atplus 419	2	31 ss	84 s	100 s	55 aa

Note: aaa is combined treatment <  $\frac{1}{2}$  sum separate treatments. aa is combined treatment < highest separate treatment. a is combined treatment < sum separate treatments - 20%. o is combined treatment = sum separate treatments  $\pm$  20%. s is combined treatment > sum separate treatments + 20%. ss is combined treatment > 2  $\times$  sum separate treatments.

into account some arbitrary classification criteria based on a comparison of the combined treatment vs. separate treatments (formulation alone or adjuvant alone), it can be stated that the fungitoxicity of the flutriafol spray was intensified by surfactants in the case of *Pythium*, but rather counteracted in the case of *Fusarium* and *Botrytis*. It is worth mentioning, however, that the latter fungi were already very effective at the experimental working conditions (1 ppm), while this concentration was rather ineffective for *Pythium*. The impact of an adjuvant was perhaps more pronounced due to a better penetration of the a.i. through the fungal cell wall. The advantageous influence of adjuvants on the activity of flutriafol against *Pythium* was suppressed for metalaxyl (Table 8). Only very slight improvements of the activities were observed, compared with the corresponding treatment without surfactant ("no surfactant"). Also, the arbitrary classification indicates an antagonistic action.

Comparison of four different formulations in combination with surfactants (Table 9) against *Pythium* generally yielded an enhanced activity of the fungicide, with the exception of metalaxyl. The same effect holds for oil adjuvants except for oxadixyl.

These few examples illustrate the complexity of the interactions involved in the influence of adjuvants on the fungitoxicity of sprays. It is possible that no general conclusions can be put forward and that prediction of the influence of adjuvants on spray performance is impossible. It has therefore already been suggested that each combination of fungicide formulation and adjuvant has to be tested for each fungus empirically in order to obtain the optimal solution.

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## Chapter 62

**STUDY ON THE PREVENTION AND CONTROL OF RED LEAF  
DISEASE ON CORN AND MILLET BY TA (TS) MIXTURE**

Er-fu Wu, Guang-rong Sun, and Ming-qi Wang

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## I. INTRODUCTION

The red leaf diseases of corn (*Zea mays* L.) and millet (*Setaria* sp.) are distributed widely over Shandong, Hebei, Ganshu, Shaanxi, Jiangshu, Anhei, and other provinces in China, and also were an important factor in the reduction of corn and millet production in other countries such as America, Japan, and India. The red leaf disease of millet has been investigated.<sup>1-3, 6</sup> Our work on the red leaf diseases of corn and millet began in 1979. The causes of these diseases were preliminarily identified as strains of barley yellow dwarf virus (BYDV) by electron microscopy and by vector aphid transmission in our laboratory, particularly the red leaf disease of corn.<sup>3, 5</sup> In 1985, we found that TA(TS) can inhibit these diseases, as well as promote the growth and development of the diseased crops. The results obtained in recent years are the content of this chapter.

## II. MATERIALS AND METHODS

TA signifies the plant growth regulator n-triacontanol  $\text{CH}_3(\text{CH}_2)_{28}\text{CH}_2\text{OH}$ , and TS is composed of TA and the surfactant Tween 80, and other ingredients.

The test corn lines were self-bred lines Va-35 and Va-107, Qi-31, and Huangzhao-4; the millets were Yegu-1, Hua-7202, Ai-7101, and Japan-60.

One experiment was conducted in pots (basins) and another in the field. In the first experiment, the basin number of every treatment was 40; there were 80 plants total, and the plants had been infected by the greenbug (*Schizaphis graminum*). In the field, every plot under treatment was 66.7 m<sup>2</sup> and contained 400 plants, which had been infected naturally. As soon as the tip leaf of the plants became red or purplish red before the jointing and earing stages of corn and millet, 0.5 ppm of TS in liquid solution was sprayed on all the leaves of the crops.

During the 3 to 14 d after spraying, the photosynthetic rate of the ears or leaf tips of 100 plants was measured randomly with an FQ-W CO<sub>2</sub> infrared analytic apparatus. The damaged chloroplasts in the leaves were observed with a microscope; the chlorophyll contents (a + b) were measured with a 751 ultraviolet spectrophotometer, and the transportation and distribution of photosynthate were analyzed with a <sup>14</sup>C-tracer method. The height and biomass of the plants were measured during the earing stage, and the ears were harvested and dried under the sun and in an oven at the maturing stage.

The virus was isolated separately from the leaves of infected, healthy, and TA(TS)-treated infected plants of corn and millet in both basins and plots, stained negatively with uranyl acetate or phosphotungstic acid, and observed with a H-500H electron microscope.

All experiments were conducted three times.

## III. RESULTS

### A. SYMPTOMS AND CAUSES OF MILLET RED LEAF DISEASE

The symptoms and causes of corn red disease have been published.<sup>5</sup> The symptoms varied with the times of infection for millet. The earlier the plants were infected, the more serious was the disease. When infected very seriously, the leaves became yellow or red and withered, and the plants became stunted and even died. Plants infected at the later period produced ears but yields were lower and the leaves were yellow and red. The virus from the infected leaves of millet was more or less icosahedral, symmetrical, and about 25 nm in diameter (Figure 1).

### B. EFFECTS OF TS ON THE YIELDS OF CORN AND MILLET

After the corn (self-bred line Va-35) in the field was treated with TS, the older leaves ceased turning red and turned green, and the young leaves were green continuously. The

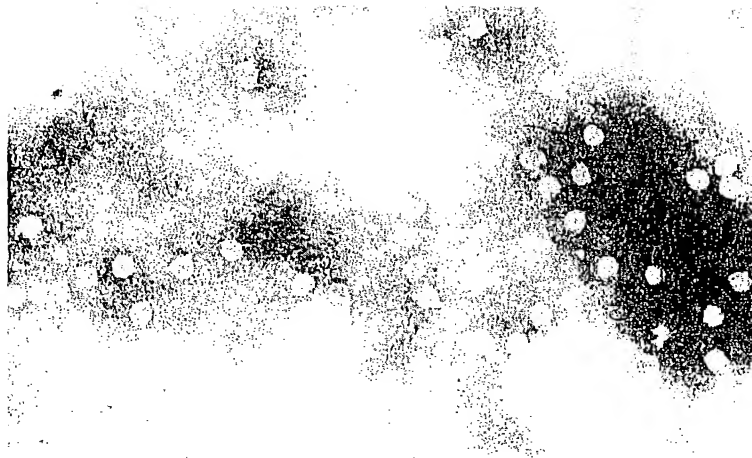


FIGURE 1. Electron micrograph of the purified virus particles of infected millet leaves, negatively stained with uranyl acetate. (Magnification  $\times 100,000$ .)

yield increased by 26.5% over the control plant. The average number of seeds on a treated ear was 187 more than the control, the weight of 1000 seeds increased by 63 g, and the economic coefficient increased from 0.19 of the control to 0.35 of the treatment. The differences were highly significant by F-value analysis.

After TS treatment, the red leaves of millet turned green, and the young leaves were green continuously. The accumulation of dry matter increased, as did biomass. The biomass of Hua-7202, Ai-7101, Japan-60, and Yegu-1 were 9.85, 7.0, 13.65, and 11.45 kg, respectively, and increased by 29.6, 41.7, 33.1, and 38.7%, respectively. F-value analysis indicated that the differences between the biomasses of treatment and control were highly significant.

### C. PHYSIOLOGICAL EFFECTS OF TS ON DISEASE-INFECTED AND DISEASE-RESISTANT BREEDS OF CORN AND MILLET

The photosynthetic rates of infected corn and millet were promoted with TS, but the extent in corn varied with hybrids and self-bred lines. Table 1 shows that the photosynthetic rate of seriously infected crops of corn (Va-35) increased by 73.9% over the control, the rate of slightly infected Huangzhao-4 by 32.2%, and the rate of the tolerant crop Qi-31 by 18.2%. The photosynthetic rate of seriously infected millet (Yegu-1) increased by 44.7% more than the control, and the rate of slightly infected Hua-7202 by 23%. The differences between the rates of treatment and control were highly significant by F-value analysis.

TS treatment without TA increased the photosynthetic rate of corn and millet breeds only slightly or not at all. The differences in comparison with the control were not significant (Table 1). Experiments using  $^{14}\text{CO}_2$  showed that the total radioactive intensity of individual TS-treated corn plants (Va-35) increased by 34.5% over the control, and the ability to assimilate  $\text{CO}_2$  increased by 18.8%. Moreover, TS promoted the transportation of photosynthate toward the ear and enhanced the absorption ability of the root (Table 2).

TS primarily affected chlorophyll content. After treatment with TS, the content (a + b) in the leaf of corn (Va-35) was 2.64 mg/dm<sup>2</sup>, an increase of 20%. In seriously infected corn (Va-107), the content (a + b) was 1.68 mg/dm<sup>2</sup>, an increase of 124%, and the content of chlorophyll b was obviously raised. The content (a + b) in the leaf of millet (Yegu-1 and Ai-7101) increased by 128 and 32.2%, respectively. Also, the content of chlorophyll

TABLE 1  
Effects of TS and TS Without TA (TS<sup>+</sup>) on Photosynthetic Rate (PR) of Corn and Millet (Spring-Sowed Plots in Field)

Breed	PR (mg CO <sub>2</sub> /dm <sup>2</sup> /h)			Increasing rate (%)		Analytic condition (position, temperature, luminosity)
	TS	TS <sup>+</sup>	Water	TS	TS <sup>+</sup>	
Corn						
Qi-1	22.46 <sup>a</sup>	19.58	19.0	18.2	3.05	Leaf of ear
Va-35	18.52 <sup>a</sup>	12.15	10.7	73.9	14.08	32°C
H.-z.-4	17.58 <sup>a</sup>	15.03	13.3	32.2	13.00	20,000 lx
Millet						
Y.-g.-1	23.3 <sup>a</sup>	17.1	16.1	44.7	6.21	Leaf tip, 32°C
H.-7202	16.2 <sup>a</sup>	14.2	13.1	23.0	8.30	20,000 lx

\* Statistically significant difference compared with the control ( $p > 0.01$ ).

Note: Values are averages of 12 measurements.

b was obviously raised. All differences between the treatment and control contents were highly significant by F-value analysis.

#### IV. DISCUSSION

In the 1950s, Yu<sup>6</sup> suggested that the cause of millet red leaf is similar to that of BYDV, on the basis of its host range and method of infection. In 1982, Matthews<sup>2</sup> identified millet red leaf virus as a member of the BYDV group according to its host range. Since 1979, the cause of corn and millet red leaf diseases has been identified in our laboratory. We found that the two diseases infect healthy plants via greenbugs from infected plants and lead to systemic infection, but not by juice and mechanical contact. Moreover, the characteristics of the causal factor, that the content of the viruses in the host varies a little and that the size of the virus is about 25 nm, were confirmed by the reports on BYDV.<sup>1,2,4,5</sup> From these studies, the causes of corn and millet red leaf diseases were identified as strains of BYDV, although the host range and serological tests have not been conducted in detail.

Over more than 3 years, we observed the infected, healthy, and TS-treated infected leaves of corn and millet in both basins and plots with an electron microscope. There were viral particles in the infected leaves, but not in healthy plants and not in the leaves treated with TS. These results may suggest that multiplication of the virus is inhibited.

TS can effectively prevent corn and millet red leaf diseases and promote the growth of the crops. Since literature on applying plant growth regulators to prevent viral diseases of plants and to enhance the antidisease capability of crops has not been seen, this perhaps may be the first report (at least in China).

Generally, the viruses of corn and millet red leaf diseases result in a drop in chlorophyll content, as in the aging of leaves.

Treatment with TS increased the chlorophyll content, enhanced the photosynthetic rate of leaves, improved the physiological conditions, and even inhibited multiplication of the viruses to some extent. Based on our other studies, enhancement of chlorophyll content may be related to plant hormones such as cytokinin. Since chlorophyll content is enhanced, photophosphorylation is reinforced, electron transfer is quickened, and accumulation of ATP as well as dry matter is increased. Consequently, all the physiological effects may delay the aging process and strengthen the resistance (antidisease capability) of the crops. Although it showed respect for an antiviral mechanism, this chapter may result in application of a

TABLE 2  
Effects of TS on Transportation and Distribution of  $^{14}\text{CO}_2$ -Photosynthate in Corn (Va-35)

Item	R (pulse/plant/min)	A (pulse $\cdot$ cm <sup>2</sup> /min)	Ear	Tassel	Husk	Root	Stem	Leaf	Sheath
TS	399291.8	689.98	106723	1624	71910.5	19287	79216	90757	7688
Water	296856.9	580.59	34239	700.4	81342.8	13454	72998	55878	7542
Incorporation rate (%)	34.5	18.8	211.7	131.9	-11.6	43.3	8.5	62.5	1.9

Note: R, radioactive intensity of individual plant; A, ability to assimilate. Values are the average of three repetitions.



plant growth regulator such as cytokinin to prevent plant viral diseases and promote the growth and development of crops.

Since TS treatment without TA could not affect the photosynthetic rate of corn and millet breeds, we suggest that TA acts as the main constituent of TS to promote photosynthesis of the crops.

TS is easy to manufacture, low in cost, applied at low concentrations, and without toxicity and contamination. TS shows great promise in preventing viral diseases and enhancing yields in crops. Further studies on the mechanism are in progress.

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## Chapter 63

**EFFECTS OF VIRUCIDE, TS, IN PREVENTING AND CURING  
TOMATO MOSAIC VIRUS DISEASE**

Er-fu Wu, Guang-rong Jinan, and Ming-qi Wang

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## I. INTRODUCTION

Tomato mosaic virus disease is currently the main cause for the decrease in tomato (*Lycopersicon esculentum* Mill.) production by more than 30% in China. As yet there is no method for preventing and curing the disease effectively in the world.<sup>2-4</sup> We found that a TS mixture can prevent and cure red leaf disease on corn (*Zea mays* L.) and millet (*Setaria* sp.) caused by barley yellow dwarf virus (BYDV).<sup>5</sup> This chapter presents results of studies on the effects of a TS mixture on the tomato mosaic disease caused by tobacco mosaic virus (TMV) and cucumber mosaic virus (CMV), and the effect of Tween 80, an adjuvant in TS, on the function of the TS mixture.

## II. MATERIALS AND METHODS

TS signifies the plant growth regulator n-triacontanol,  $\text{CH}_3(\text{CH}_2)_{28}\text{CH}_2\text{OH}$ , and the surfactant Tween 80 with other ingredients. The test plants of tomato were "Qiyanaifen" (early-ripening), "Jinfen-60" (middle-ripening), and "Qiangguangnian" (middle-ripening). The seedlings were supplied by the vegetable research institute of Shandong Province.

One experiment was conducted in pots (basins) and another in the field. In the first experiment, the basin number of every treatment was 40, and there were 80 plants in all. In the field, every plot under treatment was 33.3 m<sup>2</sup> and contained 30 plants. Each experiment was conducted three times. The experiments were continued for 4 years, beginning in 1985.

The applied concentrations of TS were 0.1, 0.5, 1.0, and 2.0 ppm in 0.07 kg/m<sup>2</sup>. The diluted TS was applied when the first inflorescence fruited, the second inflorescence flowered, and when the plants were in full fruit. The concentration of TS and the time of its application in the pot experiments were the same as in the field experiments. The experimental results were obtained at 10 and 20 d after spraying, and at the maturing stage.

Sterilized seeds were grown to seedlings in sterilized soil in a gauze-made room. The seedlings were inoculated with purified TMV and CMV by means of conventional rubbing. The TS mixture was sprayed the third day after inoculation. During 3 to 14 d after spraying, the chlorophyll content in the leaves of 100 plants was measured with a 751 ultraviolet spectrophotometer and calculated on the basis of the Arnon Y.<sup>1</sup> formula. The light reduction capacity of chloroplasts was measured by the 2,6-dichlorophenol indophenol (2,6-DCIP) method, and cytokinin (CTK) content was measured by the amaranth method.

The virus was isolated from the leaves of infected tomato plants in both basins and plots, stained negatively with uranyl acetate or phosphotungstic acid, and observed with an H-500H electron microscope on the basis of Rochow's method.<sup>4</sup>

## III. RESULTS

### A. EFFECTS OF TS ON TOMATO MOSAIC VIRUS DISEASE

The symptoms of TMV disease in the Jinan area of Shandong Province are a rolling leaf and deep, light and yellow-green spots. The cause of tomato mosaic disease was isolated, purified, and inoculated, and identified as TMV and CMV with an electron microscope (Figures 1 and 2). One application of TS on Jinfen-60 plants was 72.5% effective, and the disease index was 0.25. Two applications were 95.7% effective, with an index of 0.04 (Table 1). During 1985 to 1988, the experiments were done continually so that TS was sprayed on diseased plants of Qiyanaifen in the field plots. In 1985, the disease-prevention rate of 0.5 and 1.0 ppm TS sprayed on the leaf was 77.76 and 75.71%, respectively, and the corresponding fruit yields were increased by 12.6 and 17.3% (Table 2). In 1986, the disease-prevention rates were 92.5 and 78.3%, respectively, and the corresponding yields were increased by 10.0% and 6.7% (Table 3). During 1987 to 1988, yields were increased

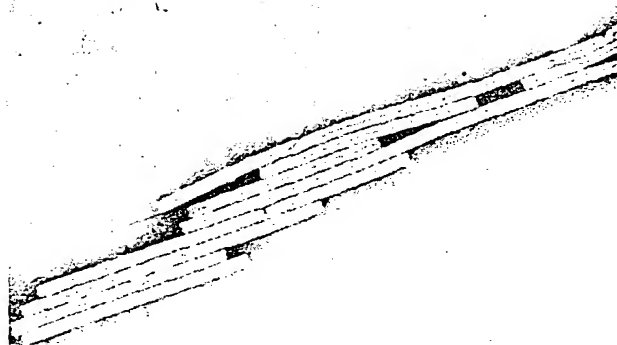


FIGURE 1. Electron micrograph of purified TMV particles of infected tomato leaves, negatively stained with uranyl acetate. (Magnification  $\times 100,000$ .)

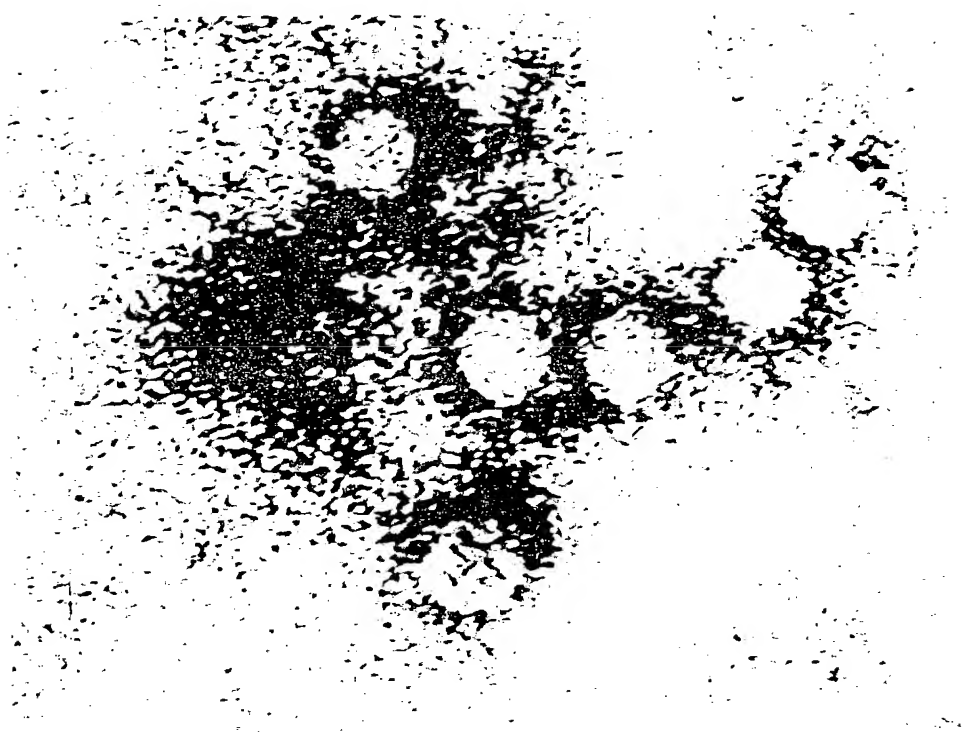


FIGURE 2. Electron micrograph of purified CMV particles of infected tomato leaves, negatively stained with uranyl acetate. (Magnification  $\times 500,000$ .)

17.0 to 23.0%. There is an exact correspondence between disease prevention and increased fruit yield of the plant.

#### B. PHYSIOLOGICAL EFFECT OF TS ON THE MOSAIC-DISEASED PLANT

Twenty days after TS treatment, the disease prevention rate was 79.10% (Table 4). Eight days after TS treatment, the CTK content of the treated plant was 337.80  $\mu\text{g/g}$  fresh leaf,

TABLE 1  
Effect of TS on Tomato Mosaic Disease of Jinfen-60 Tomatoes in Field Plots (1986)

Treatment	One application			Two applications		
	Plant number	Disease index	Effect (%)	Plant number	Disease index	Effect (%)
0.5 ppm TS	120	0.25	72.50	120	0.04	95.70
0.5 ppm TS (- Tween 80)	120	0.81	11.00	120	0.82	13.70
Water	120	0.91	—	120	0.95	—

TABLE 2  
Effect of TS on Tomato Mosaic Disease Sprayed Twice in the Field (1985)

TS (ppm)	Checked plant no.	Diseased plant no.	Diseased plants (%)	Disease-prevention rate (%)	Yield (%)	Yield-increase rate (%)
0.5	360	76	19.7	77.76*	116.2	12.6*
1.0	360	78	21.61	75.71	121.0	17.3*
0.0 (water)	360	320	88.87	—	103.2	—

\*  $F = 5.203 > F_{0.05} = 4.07$ .

TABLE 3  
Effect of TS on Tomato Mosaic Disease Sprayed Twice in the Field (1986)

TS (ppm)	Checked plant no.	Diseased plant no.	Diseased plants (%)	Disease-prevention rate (%)	Yield (kg)	Yield-increase rate (%)
0.1	190	16	7.6	78.9	125.38	4.82
0.5	198	6	2.8	92.5*	131.88	10.00*
1.0	196	16	8.3	78.3*	127.68	6.74*
2.0	193	3.4	17.4	37.7	126.73	5.33
0.0 (water)	183	70	38.5	—	119.62	—

\*  $F = 8.087 > F_{0.05} = 4.770$ .

TABLE 4  
Effect of TS on Qiyanafen Tomato Leaf Inoculated with TMV in Basins (1986)

Treatment after inoculation	Inoculation leaf no.	Diseased leaf no.	Ear no.	Pot no.	Inhibited pot rate (%)
0.5 ppm TS	20	4	2.0	0.9	79.10
0.5 ppm TS (- Tween 80)	20	12	2.1	2.0	53.50
Water	18	13	2.3	4.3	—



TABLE 5  
Effect of TS on CTK Content in Diseased  
Leaf of Qiyanaifen Tomato (1986)

Treatment	Fresh leaf weight (FW) (g)	Cytokinin content ( $\mu\text{g/g}$ FW)	Increase (%)
0.5 ppm TS	19.78	337.8	173.7
Water	19.15	123.4	

TABLE 6  
Effect of TS on Chlorophyll Content of Qiyanaifen Tomato Leaf in Basins (1986)

Treatment	Chlorophyll a (mg/g FW)	Chlorophyll b (mg/g FW)	Chlorophyll a + b (mg/g FW)	Increase (%)
0.5 ppm TS	0.9156	0.3231	1.2387	17.62
0.5 ppm TS (- Tween 80)	0.8990	0.2330	1.1320	7.49
Water	0.7716	0.3414	1.0531	—

Note: FW, fresh leaf weight.

TABLE 7  
Effect of TS on Reducing DCIP Capacity for Qiyanaifen Chloroplasts  
in Plots (1986)

Treatment	Chlorophyll (a + b) (mg/g FW)	DCIP (mg/ml)	Reducing DCIP capacity (ml/mol/mg chlorophyll per h)	Increase (%)
0.5 ppm TS	1.50	0.0084	300	78.5
0.5 ppm TS (- Tween 80)	1.30	0.0059	184	8.3
Water	1.23	0.0053	168	—

Note: Under 20K lx of light intensity, FW, fresh leaf weight.

the content of the water-treated plant was 123.4  $\mu\text{g/g}$  fresh leaf, and the rate of increase of CTK was 173.70% (Table 5). This indicates that the disease-prevention effect of TS on tomato mosaic disease may be related to the CTK increase in the leaf.

Table 6 shows that the TS mixture substantially affected the chlorophyll content of the tomato plant. The content under TS treatment increased by 17.62%, which in turn could reinforce the photosynthesis of the plant and the accumulation of organic matter *in vivo*.

Table 7 shows that 0.5 ppm TS obviously increased the chlorophyll content of infected leaves and that the DCIP-reducing capacity increased by 78.5%.

### C. CONTRIBUTION OF TWEEN 80 TO DISEASE PREVENTION AND PHYSIOLOGICAL EFFECTS OF TS

Tables 1 and 4 show that Tween 80 raised the disease-prevention effect of TS on the diseased plant from 13.70 to 95.70%, and on the infected leaf from 53.50 to 79.10%. Moreover, Tween 80, increased the effect of TS on the chlorophyll content of the infected leaf from 7.49 to 17.62% (Table 6), and on the DCIP-reducing capacity of the leaf from 8.3 to 78.5% (Table 7).

#### IV. DISCUSSION

Since 1985, the cause of tomato mosaic disease in the Jinan area of the Shandong Province in China has been identified as TMV and CMV. There have been additional reports on the shape and structure of the viruses, but few on preventing and curing the disease chemically.<sup>6</sup> Our experiments showed that spraying 0.5 to 1.0 ppm TS on tomato plants infected artificially in basins and infected naturally in plots at the first flowering and 15 d later resulted in a disease-prevention rate of 95.7%. Yields were increased by an average of 17.3%. When spraying TS at the TMV-infecting stage, the infection and duplication of the virus are inhibited to some extent, the growth and development of healthy plants are promoted, and this disease resistance is reinforced. This provides a new way of preventing and curing the plant virus disease and increasing tomato yield.

The main physiological effects of TS on the diseased plant were the increase of chlorophyll and CTK content, enhancement of the light reduction capacity of chloroplasts, and improvement of the physiological state of the plant. The virus decreases chlorophyll content, inhibits growth and development of the plant, and photosynthesis drops. The disease-prevention effect of TS on the disease caused by TMV is related to the chlorophyll and CTK content. Each TS treatment increases chlorophyll content on an average of 17.62%; light reduction capacity of chloroplasts, 78.5%, and CTK content, 173.70%. On the basis of these results, we concluded that promoting the growth and development of the plant is consistent with preventing and curing the virus disease of the plant.

As an adjuvant, Tween 80 substantially increases the effects of TS on the tomato mosaic virus disease. We think that Tween 80 as a surfactant could promote the permeation of the other components in TS into the leaf.

TS has the same effects on different varieties of tomato. Application of 0.5 ppm TS at the first flowering is effective, but when the disease becomes more serious, 1.0 ppm TS should be applied. Generally, TS is applied twice at 15-d intervals. TS is effective in preventing and curing vegetable mosaic virus diseases in the south and north of China.

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## Chapter 64

**EFFECT OF PINOLENE AS AN ADJUVANT TO IPRDIONE FOR  
CONTROL OF SCLEROTINIA BLIGHT OF PEANUT**

F. D. Smith, P. M. Phipps, and R. J. Stipes

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## ABSTRACT

Pinolene, a pine resin derivative containing 96% di-1-*p*-menthene, improved the performance of iprodione for control of Sclerotinia blight of peanut caused by *Sclerotinia minor*. Average yields during 1985 to 1989 from test plots treated on demand with iprodione (1.12 kg/ha) and pinolene at 0.18% (v/v) in a spray volume of 335 l/ha were 365 kg/ha higher and disease incidence 15% lower than plots treated with iprodione alone. Treatments were applied three times in 1985, 1986, and 1987, and twice in 1988 and 1989. The additional value of peanuts obtained each year with the addition of pinolene to iprodione was \$298/ha, whereas the cost of using pinolene was \$7.22/ha. These results were significant ( $p = 0.05$ ) when examined over the 5-year period. Pinolene enhanced, but not significantly, the performance of chlorothalonil (1.26 kg/ha) for control of *Cercospora* leafspot of peanut caused by *Cercospora arachidicola*. Sprays were applied according to the Virginia peanut leafspot advisory program and averaged 4.5 applications per season. Pinolene may have failed to enhance performance of chlorothalonil due to the high level of disease control with chlorothalonil alone.

## I. INTRODUCTION

The purpose of adjuvants is to improve the physical properties of a pesticide mixture, thereby enhancing the efficacy of the spray. Because of renewed environmental interest and increasing concerns over the alleged health effects of agrichemical residues in the food supply, many fungicide applications are being made at the lowest effective dose and only when conditions are conducive for disease development. Adjuvants have the potential to increase the effectiveness of agrichemicals, enabling the reduction of application rates or number of sprays.

Sclerotinia blight, caused by *Sclerotinia minor* (Jagger) Kohn,<sup>5</sup> currently claims 4 to 8% of the peanut crop in Virginia each year.<sup>9</sup> Iprodione is a dicarboximide fungicide and has been labeled for control of Sclerotinia blight since 1985. Currently, use of this fungicide is the favored method of controlling Sclerotinia blight of peanut in Virginia. The dicarboximides function as protectant fungicides with activity against representatives of the following genera of fungi: *Botrytis*, *Sclerotinia*, *Monilinia*, *Alternaria*, *Sclerotium*, and *Phoma*.<sup>13</sup> Control of Sclerotinia blight incidence with iprodione commonly averages 45 to 55% and has resulted in a need for more efficacious control strategies.<sup>2</sup> The disease is first detectable at the soil surface and under the dense peanut canopy. The well-concealed location of infections is often not detected in time for the effective use of fungicides. Applications of iprodione should commence when the disease becomes active and thereafter at 4-week intervals for a total of not more than three times.<sup>10</sup> Between the 4-week spray intervals, Sclerotinia blight can become active if the weather remains cool and wet for an extended time.

Sclerotinia blight was first detected in the Virginia-North Carolina area in 1971<sup>14</sup>. Since that time, the disease has been reported in other peanut-producing areas of the country, such as Oklahoma,<sup>18</sup> New Mexico, and Texas.<sup>17</sup> The rapid spread of the disease has the potential to substantially reduce national peanut yields unless current control measures are improved. Since pinolene was relatively nontoxic to animals<sup>3</sup> and was reported to enhance the performance of chlorothalonil for control of peanut foliar diseases,<sup>15</sup> it was included in a test of adjuvants with iprodione for control of Sclerotinia blight. Pinolene was also evaluated as an adjuvant with chlorothalonil for control of *Cercospora* leafspot of peanut caused by *Cercospora arachidicola* Hori. Recent losses to *Cercospora* leafspot have averaged 4% of the potential peanut crop in Virginia.<sup>9</sup>

Chemically, pinolene contains 96% di-1-*p*-menthene. It is derived from pine resin and forms a terpenic polymer after application. The material has been promoted as an extender-sticker-spreader which surrounds and holds the pesticide on sprayed areas of the plant. Pesticide life is extended by negating the effects of environmental damage, such as rainfall, wind erosion, photodecomposition, volatilization, and heat destruction, thus prolonging the active life of most pesticides by 25 to 50%. Pinolene has been promoted as effective when used with fungicides such as anilazine, captafol, chlorothalonil, maneb, and zineb.<sup>7</sup>

The use of spray adjuvants does not always enhance plant disease control. Although adjuvants usually lack fungicidal properties, adjuvants do have the potential to alter the plant cuticle which forms the major barrier against biotic and nonbiotic insults. The application of some spray adjuvants without a fungicide significantly increased the development of disease in grapes caused by *B. cinerea*.<sup>6</sup> There was a significant correlation between water loss from grapes and disease development, which indicated that the increase in disease was due to disruption of the normal function of the epicuticular waxes on the berry. Most of the adjuvants that enhanced disease development contained petroleum oils. These oils may have contributed to the removal of protective waxes from the grapes. Pinolene lacks additional oils and was not reported to increase disease development on treated grapes.

Since Sclerotinia blight has proved to be a difficult disease to control with registered fungicides, research on adjuvants may provide a much-needed means for improved disease management. The development and registration of fungicides with greater efficacy against *S. minor* than iprodione,<sup>16</sup> as well as biological control agents, will take years of additional research. Adjuvants may help to fill the void of compounds that are extremely effective in controlling Sclerotinia blight by improving the performance of currently available fungicides.

## II. MATERIALS AND METHODS

### A. ADJUVANTS AND FUNGICIDES

Ten adjuvants, representing a wide range of ingredients, were evaluated in 1985 for their activity with iprodione (Rovral®, Rhône-Poulenc, Research Triangle Park, NC). Pinolene (Nu-Film-17®) and Spray-Aide® were obtained from Miller Chemical and Fertilizer Corp., Hanover, PA. Spray-Aide is an acidifying surfactant containing 70% alkylaryl polyoxyethylene glycol phosphate ester. Acetic acid and hydrochloric acid were obtained as technical grade chemicals, and were tested to determine the effects of lowered pH on the performance of iprodione. Chem-Oil 83®, ChemWett Plus®, and SoyOil 937® were obtained from Coastal Chemical Corp., Greenville, NC. Chem-Oil 83 is an 83% paraffin-based petroleum oil with surfactants, and is thought to function mainly as a surfactant. ChemWett Plus contains 80% alkylaryl polyethylene glycols and organic solvents, and is classified as a spreader and activator. SoyOil 937 contains 93% soybean oil and 7% emulsifier. Agri-Dex®, Buffer P.S.,® and Penetrator-3® were obtained from Helena Chemical Co., Memphis, TN. Agri-Dex is a mixture of heavy-range paraffin-based petroleum oil, polyol fatty acid esters, and their polyethoxylated derivatives that function as spreaders, stickers, and/or penetrants. Buffer P.S. contains 30% alkylaryl polyethoxy ethanol phosphates and organic phosphatic acids, and is classified as a spreader and buffering agent. Penetrator-3 is a 98% mixture of paraffin-based petroleum oil, polyol fatty acid esters, and their polyethoxylated derivatives, and functions mainly as a penetrant.

### B. FIELD TRIALS

Peanuts (cvs. Florigiant during 1985 to 1987 and NC-9 during 1988 to 1989) were planted and managed according to standard practices for peanut production in Virginia.<sup>10</sup> Treatments to evaluate fungicide sprays with and without adjuvants were applied to the two center rows of four-row plots using a CO<sub>2</sub>-pressurized backpack sprayer. The adjacent outer rows of each plot functioned as guard rows. The experimental design consisted of four



randomized complete blocks with 12.2-m rows spaced 0.9 m apart. Each block was separated by a 2.1-m alleyway. Disease incidence was monitored monthly and recorded as the number of infection centers in the center rows of each plot.<sup>11</sup> Yields were based on the weight of harvested peanuts from the two center rows and a moisture content of 7% (w/w). Values were determined from a 500-g composite sample from each treatment, in accordance with Federal-State Inspection Service methods. Statistical analyses on disease incidence, yield, and value were determined by Duncan's new multiple range test using a probability value of 0.05.

Ten adjuvants were individually evaluated with iprodione (1.12 kg/ha), as Rovral 50WP, in 1985 for control of Sclerotinia blight in a field having a history of severe Sclerotinia blight. Treatments were applied three times (July 18, August 14, and September 12) using two different spray methods. High-pressure, low-volume sprays were delivered at 140 l/ha with three D<sub>2</sub>13 (disk-core combination) nozzles per row and a pressure of 345 kPa. Low-pressure, high-volume sprays were applied at 335 l/ha with one 8008LP nozzle per row at 165 kPa. As commonly recommended by manufacturers of spray adjuvants, rates are expressed as percent of spray volume. At 140 l/ha, adjuvants and rates (v/v) included: 0.83 N acetic acid, 1.0%; Agri-Dex, 0.83%; Buffer P.S., 0.13%; Chem-Oil 83, 0.83%; ChemWett Plus, 0.83%; 1 N HCl, 0.75%; pinolene, 0.42%; Penetrator-3, 0.42%; SoyOil 937, 1.0%; and Spray-Aide, 0.06%. At 335 l/ha, adjuvants and rates were: 0.83 N acetic acid, 1.0%; Buffer P.S., 0.13%; 1 N HCl, 0.70%; pinolene, 0.18%; SoyOil 937, 0.42%; and Spray-Aide, 0.06%.

Subsequent tests during the next four years (1986 to 1989) focused on the use of pinolene with iprodione. Due to formulation changes by the manufacturer, iprodione was used as Rovral 50WP in 1986, 1987, and 1988, and as Rovral 4F in 1989. Treatments were applied using only 8008LP nozzles calibrated to deliver 335 l/ha at 165 kPa. Iprodione was applied at 1.12 kg/ha with and without pinolene at 0.18% (v/v) at 4-week intervals after Sclerotinia blight became active in the field. Three applications were made in 1986 (July 10, August 7, and September 4) and 1987 (July 31, August 28, and September 25). Two applications were made in 1988 (August 3 and September 1) and 1989 (July 20 and August 16).

Pinolene was also evaluated as a spray adjuvant with chlorothalonil (Bravo® 720, Fermenta Agricultural Specialty Chemicals, Mentor, OH) for control of Cercospora leafspot of peanut. During 1986 to 1989, treatments were applied with three D<sub>2</sub>13 nozzles over each row. Total spray volume was 335 l/ha. Plots were untreated, treated with chlorothalonil at 1.26 kg/ha and pinolene 0.42% (v/v), or chlorothalonil alone. Sprays were applied according to the Virginia peanut leafspot advisory program<sup>12</sup> and averaged 4.5 applications per season.

### III. RESULTS

#### A. PRELIMINARY EVALUATION OF ADJUVANTS

The application of iprodione alone with D<sub>2</sub>13 nozzles did not significantly suppress disease incidence in 1985 (Table 1). However, the addition of several different spray adjuvants to iprodione resulted in significant disease suppression. Disease incidence was suppressed by 49, 48, 48, 36, and 33% in plots treated with iprodione containing the adjuvants Spray-Aide, ChemWett Plus, pinolene, 1 N HCl, and Chem-Oil 83, respectively. When 8008LP nozzles were used, iprodione alone significantly suppressed disease incidence by 33%. The addition of spray adjuvants to iprodione improved the performance of the fungicide, as disease incidence was suppressed by 47, 40, 37, and 37% in plots treated with iprodione containing pinolene, SoyOil 937, Buffer P.S., and Spray-Aide, respectively.

All applications of iprodione with and without various adjuvants produced significant yield increases in peanut as compared to untreated peanuts, with the exception of Agri-Dex. Although not significantly better than iprodione alone, pinolene was the best-performing

**TABLE 1**  
**Comparison of Spray Adjuvants Used With Iprodione**  
**for Control of Sclerotinia Blight of Peanut in 1985**

Treatment and adjuvant rate (v/v) <sup>a</sup>	Disease incidence (hits/plot) <sup>b</sup>	Yield (kg/ha) <sup>c</sup>
Untreated check	49.0 a	2875 c
Three D <sub>2</sub> 13 nozzles per row		
Iprodione (1.12 kg/ha) alone	34.5 a-c	3847 ab
+ 0.83 N Acetic acid, 1.0%	39.5 a-c	3758 ab
+ Agri-Dex, 0.83%	44.3 ab	3405 bc
+ Buffer P.S., 0.13%	37.0 a-c	3783 ab
+ Chem-Oil 83, 0.83%	32.8 bc	3682 ab
+ ChemWett Plus, 0.83%	25.3 c	3922 ab
+ 1 N HCl, 0.75%	31.5 bc	3960 ab
+ Pinolene, 0.42%	25.5 c	4111 ab
+ Penetrator-3, 0.42%	36.0 a-c	3607 ab
+ SoyOil 937, 1.0%	37.5 a-c	3758 ab
+ Spray-Aide, 0.06%	24.8 c	3783 ab
One 8008LP nozzle per row		
Iprodione (1.12 kg/ha) alone	33.0 bc	3884 ab
+ 0.83 N Acetic acid, 1.0%	37.3 a-c	3720 ab
+ Buffer P.S., 0.13%	30.8 bc	3821 ab
+ 1 N HCl, 0.70%	36.8 a-c	3884 ab
+ Pinolene, 0.18%	26.0 c	4338 a
+ SoyOil 937, 0.42%	29.3 bc	4035 ab
+ Spray-Aide, 0.06%	31.0 bc	3809 ab

Note: Means followed by the same letter(s) are not significantly different at  $p = 0.05$  according to Duncan's new multiple range test.

<sup>a</sup> Three applications were made (July 18, August 14, and September 12). Spray volumes were 140 l/ha with D<sub>2</sub>13 nozzles or 335 l/ha with 8008LP nozzles.

<sup>b</sup> Disease incidence represents the number of infection centers in two 12.2-m rows at harvest.

<sup>c</sup> Yield based on weight of peanuts adjusted to 7% moisture (w/w).

spray adjuvant based on peanut yield, regardless of the application method. Peanuts treated with iprodione and pinolene using D<sub>2</sub>13 and 8008LP nozzles yielded 264 and 454 kg/ha more, respectively, than peanuts similarly sprayed with iprodione alone. During tests of similar adjuvants in 1986, pinolene was again the best-performing fungicide adjuvant, based on peanut yield.<sup>8</sup> Since pinolene showed a trend of enhancing the performance of iprodione using two different methods of spray applications and performed well during two seasons, pinolene was chosen for continued evaluation.

#### B. EVALUATION OF PINOLENE WITH IPRODIONE FROM 1985 TO 1989

Application of iprodione alone did not significantly suppress Sclerotinia blight during 2 of 5 years, 1986 and 1987 (Table 2). The addition of pinolene to iprodione resulted in significant disease control during all 5 years of evaluation. Disease incidence at harvest was 21, 20, 13, and 15% less in plots treated with iprodione and pinolene compared to treatment with iprodione alone in 1985, 1986, 1987, and 1989, respectively. Addition of pinolene to the fungicide spray did not limit disease incidence in 1988. Yearly differences in disease incidence in plots treated with iprodione and pinolene or iprodione alone were not statistically significant. Analysis of the combined results of field research over the 5-year period indicated

TABLE 2  
Control of Sclerotinia Blight of Peanut with and without  
Pinolene as an Adjuvant to Iprodione

Year and treatment <sup>a</sup>	Disease incidence <sup>b</sup> (hits/plot)	Yield <sup>c</sup> (kg/ha)	Value <sup>d</sup> (\$/ha)
1985			
Iprodione + pinolene	26.0 b	4338 a	3002 a
Iprodione	33.0 b	3884 a	2654 a
Untreated	49.0 a	2875 b	1938 b
1986			
Iprodione + pinolene	30.0 b	3176 a	2227 a
Iprodione	37.5 ab	2745 ab	1847 a
Untreated	44.8 a	1932 b	1281 b
1987			
Iprodione + pinolene	18.3 b	5441 a	3714 a
Iprodione	21.0 ab	5112 ab	3489 a
Untreated	29.5 a	4768 b	3247 a
1988			
Iprodione + pinolene	30.3 b	3093 a	2175 a
Iprodione	27.5 b	3202 a	2257 a
Untreated	47.8 a	1914 b	1316 b
1989			
Iprodione + pinolene	5.5 b	4411 a	3109 a
Iprodione	6.5 b	4284 a	2891 a
Untreated	15.5 a	4253 a	2958 a
5-Year Average			
Iprodione + pinolene	21.6 c	4144 a	2880 a
Iprodione	25.3 b	3779 b	2582 b
Untreated	37.3 a	3148 c	2148 c

Note: Means followed by the same letter(s) within a given period are not significantly different at  $p = 0.05$  according to Duncan's new multiple range test.

<sup>a</sup> Three applications using one 8008LP nozzle per row at 335 l/ha were made in 1985, 1986, and 1987; two applications were made in 1988 and 1989. Iprodione was applied at 1.12 kg/ha and pinolene at 0.18% (v/v).

<sup>b</sup> Disease incidence represents the number of infection centers in two 12.2-m rows at harvest.

<sup>c</sup> Yields based on weight of peanuts adjusted to 7% moisture (v/v).

<sup>d</sup> Value was determined from a 500-g composite sample from each treatment in accordance with Federal-State Inspection Service methods.

a significant improvement in disease control by the use of pinolene as an adjuvant with iprodione. During this period, plots treated with both iprodione and pinolene had 15% less disease compared to plots treated only with iprodione.

Use of iprodione alone increased yields significantly during only 2 of 5 years, whereas use of iprodione and pinolene significantly increased yields during 4 of 5 years compared to untreated plots. Yields from plots treated with both iprodione and pinolene averaged 454, 431, 329 and 127 kg/ha more for years 1985, 1986, 1987, and 1989, respectively, than plots treated with iprodione alone. No increase in yield was attributed to use of pinolene in 1988. The effects on yield and crop value by the addition of pinolene to iprodione were not significant when analyzed for each individual year, but were significant when examined over the 5-year period. During 1985 to 1989, average yields were increased by 365 kg/ha, which represented an additional value in peanuts of \$298/ha.

### C. EVALUATION OF PINOLENE WITH CHLOROTHALONIL

Pinolene enhanced, but not significantly, the performance of chlorothalonil for control of *Cercospora* leafspot of peanut as determined by the incidence of leafspot and peanut yield in tests from 1986 to 1989. Yields averaged 4363, 4255, and 3362 kg/ha for plots treated with chlorothalonil and pinolene, chlorothalonil alone, and untreated, respectively. Use of pinolene as an adjuvant reduced the incidence of infected leaflets from 7.4 to 3.8%. Untreated plots averaged 73.9% diseased leaflets. The increase in peanut yield of 108 kg/ha obtained with the addition of pinolene to chlorothalonil had an additional value of \$129/ha.

## IV. DISCUSSION

The use of pinolene as a spray adjuvant significantly improved peanut yields by increasing the efficacy of iprodione for controlling Sclerotinia blight of peanut during a 5-year test period. The addition of pinolene to iprodione also resulted in more consistent performance of this fungicide. During each year, plots treated with iprodione and pinolene had significantly less disease than untreated plots. These findings have resulted in the recommendation for Virginia peanut growers to use pinolene (Nu-Film-17) with iprodione for control of Sclerotinia blight.<sup>10</sup> The average cost of using pinolene with iprodione was \$2.77/ha for each application. During the period, the average seasonal cost associated with use of pinolene was \$7.22/ha, and the additional value of peanuts was \$298/ha. Thus, the use of pinolene appeared to be cost effective.

Iprodione with pinolene performed well during 1985 through 1987, with yield improvements attributed to use of the adjuvant ranging from 329 to 454 kg/ha. However, no yield improvement was obtained with the addition of pinolene to iprodione in 1988, and only a small improvement of 127 kg/ha was seen in 1989. During 1988 and 1989, only two applications of iprodione were made; three treatments were made in previous years. The reduction in fungicide treatments may have limited the availability of iprodione during critical periods for disease control.

Varying the application method of fungicides by using D<sub>2</sub>13 nozzles at a spray rate of 140 l/ha or 8008LP nozzles at 335 l/ha did not significantly change the performance of iprodione alone or iprodione and pinolene during 1985, based on peanut yield. Thus, either spray technique appeared to be effective in delivering iprodione. Once the fungicide reaches the site of deposition, pinolene apparently functions more as an extender and stickier than as a spreader. If pinolene were functioning mainly as a spreader, greater differences in performance would have been expected between the two methods of spray application.

According to Miller Fertilizer and Chemical Co. literature, pinolene functions at first as a stickier to prevent losses of fungicide from rainfall. This occurs after polymerization of di-1-*p*-menthene, which is the active ingredient in pinolene. The active ingredient is also thought to act as an extender since the polymerized pinolene suppresses the oxidation and hydrolysis reactions of fungicide degradation. This role of pinolene may be important because the heterocyclic ring structure of iprodione is susceptible to base-catalyzed reactions and rearrangement with loss of fungicidal activity.<sup>4</sup> Iprodione will begin to degrade in an aqueous suspension above pH 7 after 12 h.<sup>1</sup> Depending on the weather and growth stage of peanuts, fungicides can be exposed to high levels of UV light and high temperatures that catalyze undesirable chemical reactions.

Pinolene improved the performance of iprodione so that the iprodione and pinolene treatments always had significantly less disease incidence than the untreated check. This improvement makes the use of the fungicide somewhat more environmentally tolerable because iprodione with pinolene has a higher ratio of benefit to amount of applied fungicide. The use of other spray adjuvants did not greatly alter the performance of iprodione for control of Sclerotinia blight. The acidifying agents, 0.83 N acetic acid, 1 N HCl, and Spray-



Aide, reduced the pH of tank mixes of iprodione from 7.6 to 5.6, 5.5, and 6.5, respectively. The change in pH had no significant effect on the performance of iprodione for control of Sclerotinia blight of peanut, suggesting that decomposition of iprodione in mildly alkaline water was not a serious problem. The two adjuvants containing petroleum oils and classified as penetrants,<sup>6</sup> Agri-Dex and Penetrator-3, were the poorest-performing adjuvants, based on peanut yield. Disruption of the plant cuticle may be responsible for increased susceptibility to infection.<sup>6</sup> In addition, a damaged cuticle may have allowed the fungicide to wash off more easily.

The inability to show a significant enhancement of disease control or yield with the addition of pinolene to chlorothalonil for control of Cercospora leafspot of peanut may have been due to the high level of disease control obtained with chlorothalonil alone. Research with pinolene and chlorothalonil in Texas during 1975 showed a significant enhancement of fungicide performance with the addition of the adjuvant, as plots treated with chlorothalonil and pinolene had an 18.9% incidence of leafspot compared to 28.5% in plots treated with chlorothalonil alone.<sup>15</sup> This high incidence of leafspot in fungicide-treated plots indicated only partial control of leafspot. Untreated plots averaged 80.0% diseased leaflets. Applying fungicide applications during periods that are conducive to leafspot development, based on the Virginia Peanut Leafspot Advisory, and improvements in the formulation of chlorothalonil have greatly improved the current level of disease control. Future research on leafspot control with chlorothalonil and spray adjuvants should employ reduced rates of chlorothalonil.

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## Chapter 65

**ADJUVANT EFFECTS OF SOYOIL 937® ON FUNGICIDES FOR  
CONTROL OF EARLY LEAFSPOT AND SCLEROTINIA BLIGHT  
IN PEANUTS****R. M. Cu, Patrick M. Phipps, and R. J. Stipes****TABLE OF CONTENTS**

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## ABSTRACT

SoyOil 937® (93.7% soybean oil and 6.3% emulsifiers; Coastal Chemical Corp., Greenville, NC) at rates of 0, 0.7, 1.4, 2.8, and 5.6 l/ha was evaluated for adjuvant effects on physical spray characteristics of chlorothalonil. The rates corresponded to 0, 0.5, 1, 2, and 4% of the spray volume (140 l/ha). SoyOil 937 was tested with chlorothalonil and iprodione for control of early leafspot (*Cercospora arachidicola*) and Sclerotinia blight (*Sclerotinia minor*), respectively. Chlorothalonil (Bravo 720®) with various adjuvant concentrations was applied with D<sub>2</sub>13 nozzles and 345 kPa pressure for control of early leafspot. Iprodione (Rovral 50W®) with adjuvant at 1% of the spray volume (335 l/ha) was applied with 8008LP nozzles and 165 kPa pressure. The addition of adjuvant at various rates to Bravo 720 did not alter spray volume, but the contact angle of spray droplets decreased as adjuvant levels increased. These results suggested an improvement in wettability of leaf surface. The frequency polygon for deposits of spray droplets approached a Gaussian distribution with a mean diameter of 255.4 µm. As the level of SoyOil 937 was increased, the distribution curve shifted toward a larger size in droplets. Leafspot incidence in field trials exhibited a quadratic polynomial curve with increasing levels of adjuvant up to 2% of spray volume in sprays of chlorothalonil. SoyOil 937 at rates of 0.5 and 1% of spray volume significantly improved leafspot control with chlorothalonil at 1.26 kg/ha, and was significantly better than chlorothalonil alone or at reduced rates with any level of adjuvant. The disease control efficacy of full and reduced rates of chlorothalonil was reduced significantly ( $p = 0.05$ ) with adjuvant at 4% of spray volume. The performance of iprodione for control of Sclerotinia blight of peanut was not affected significantly by the use of SoyOil 937.

## I. INTRODUCTION

Spray adjuvants have long been advocated for enhancement of pesticide performance in crop protection. Included in the broad definition of spray adjuvants are various spray additives representing diverse types of chemistry. They are generally classified as surfactants, stabilizing agents, deposit builders, foam and antifoam agents, buffering agents, activators, and others.<sup>6</sup> Oil is another class of spray adjuvant that includes crop oil and oil concentrates. Members of each class of spray adjuvant have a unique type of action that is generally common to a class. Some spray adjuvants may also perform other types of action or impart attributes belonging to other classes of adjuvants. The classification of adjuvants based on their type of action is not mutually exclusive.<sup>6</sup> Crop oil may improve droplet distribution,<sup>1</sup> enhance translocation or systemic activity,<sup>3,12</sup> increase the area of spray coverage,<sup>1</sup> improve cuticular or translaminar penetration,<sup>5,12</sup> and offer some resistance to wash-off by rain.<sup>2</sup> All of these factors can be expected to improve the herbicidal and insecticidal properties of pesticides. The addition of adjuvants to sprays of fungicides, however, has resulted in inconsistent results. Some adjuvants are known to enhance the performance of some fungicides, while others enhance the severity of disease.<sup>9</sup> Before an adjuvant can be recommended with a fungicide, the fungicide-adjuvant preparation should be evaluated for effects on physical spray characteristics and disease control efficacy.

Chlorothalonil and iprodione were selected as test fungicides because of their importance in the control of early leafspot and Sclerotinia blight of peanut caused by *Cercospora arachidicola* Hori and *Sclerotinia minor* Jagger, respectively. The former fungicide is used widely in Virginia against early leafspot, and the application is timed according to the Virginia Peanut Leafspot Advisory program.<sup>4,11</sup> The application of fungicides according to the advisory program has reduced the number of sprays from seven on a 14-d spray program to an average of 3.5 per season. In spite of the reduced number of spray applications, the advisory program has been used to achieve disease control that is comparable to spraying

on a 14-d schedule. The advisory program requires that an effective fungicide be available for control of early leafspot, and that the material be applied correctly at proper times during the growing season. Improvements in application technique, fungicide formulation, or physical attributes of sprays are needed to improve further the performance of the fungicide and increase the confidence growers will have in the program. The use of spray adjuvants could possibly enhance the performance of chlorothalonil through either improvement of efficacy in disease control or maintenance of the current level of disease control at a reduced rate of fungicide. The former may reduce the potential yield loss attributed to leafspot disease, while the latter may reduce the total fungicide input.

The need to improve the performance of fungicides to control early leafspot as well as the need to improve the performance of fungicides for Sclerotinia blight control through the use of an adjuvant, prompted the evaluation of SoyOil 937 (a soybean oil adjuvant). The objectives of the study were: (1) to evaluate the adjuvant properties of SoyOil 937 at various rates on physical spray characteristics of chlorothalonil, (2) to determine the optimum rate of SoyOil 937 with chlorothalonil for enhanced leafspot control, and (3) to test the adjuvant effect of SoyOil 937 on iprodione for enhanced Sclerotinia blight control. The study will provide information on the utility of soybean oil as an adjuvant for fungicides that are commonly used to control the two major diseases of peanuts in Virginia, *Cercospora* leafspot and Sclerotinia blight. The use of spray adjuvant with fungicides will also explore the possibility of reducing fungicide rates without compromising disease control.

## II. MATERIALS AND METHODS

SoyOil 937 at rates of 0, 0.7, 1.4, 2.8, and 5.6 l/ha was evaluated as an adjuvant for Bravo 720, a flowable formulation of chlorothalonil containing 720 g of active ingredient (a.i.) per liter (Fermenta Plant Protection, Painesville, OH). These rates corresponded to 0, 0.5, 1, 2, and 4% of the spray volume (140 l/ha). Determinations of Bravo 720 spray characteristics with and without adjuvant included measurements of droplet contact angle, spray discharge, area of spray coverage, and droplet size after deposition. Adjuvant effects on the fungicidal activity of Bravo 720 and Rovral 50W (iprodione, Rhône-Poulenc, Research Triangle Park, NC) were evaluated in field plots.

### A. EFFECTS OF SOYOIL 937 ON DROPLET CHARACTERISTICS

Droplet-to-surface interaction was assessed by measurement of the contact angle on a flat waxy surface that resembled a peanut leaf. The contact angle of water on the third fully expanded leaf from the apex of the main stem of peanut (cv. Florigiant) was measured using a Model 100-00 Contact Angle Goniometer (Ramé-Hart, Inc., NJ). A flat, durable material with about the same water contact angle as the leaf was needed to simulate a peanut leaf in droplet contact angle studies involving increasing rates of adjuvant. Paraffin, polyethylene, and polypropylene were tested to find a substitute for peanut leaves. A paraffin-coated slide was used as the stage in the humidified chamber of the goniometer. The spray droplet contact angle for Bravo 720 at 12.5 ml/l of spray volume was measured with SoyOil 937 at levels of 0, 0.5, 1.0, 2.0, and 4.0% of spray volume. Contact angles were transformed to cosine  $\theta$  prior to statistical analysis.

Droplet size, droplet distribution, and the area of spray coverage were determined after spraying different adjuvant concentrations on grided transparency film using a CO<sub>2</sub>-pressurized sprayer equipped with D<sub>2</sub>13 (disc-core combination) nozzles. The fungicide-adjuvant preparations were sprayed at 345 kPa and a speed of 1.2 m/s. Spray pressure, speed, and volume per unit area approached that for field application. The droplets per grid area were counted with the light microscope, and the diameter of 100 systematically selected droplets was measured with an ocular micrometer. Spray droplet distribution was described by the

number of droplets per square centimeter and the occurrence of droplets in various size categories. These data were used to develop a frequency polygon showing the mean, median, and mode of droplet. Spray coverage was calculated from the ratio of the area covered by the droplets (product of the number of droplets per grid and mean droplet size) to the area of the grid.

## B. FIELD EVALUATION

Florigiant peanut was planted in a Kenansville loamy sand with a corn-peanut history of crop rotation at the Tidewater Agricultural Experiment Station, VPI & SU, Suffolk, VA. Cultural practices recommended by the Virginia Cooperative Extension Service were followed in crop management.<sup>14</sup> Bravo 720 was evaluated at rates of 0, 0.44, 0.88, and 1.75 l/ha in 1987, and 0, 0.88, 1.32, and 1.75 l/ha in 1988. SoyOil 937 was tested at 0, 0.5, 1.0, 2.0, and 4.0% of spray volume (140 l/ha). Rovral 50W at 2.24 kg/ha with SoyOil 937 at 1% of spray volume was tested in a field with a history of Sclerotinia blight. Treatments were applied to the two center rows of each plot. Plots consisted of four 12-m rows spaced 0.9 m apart. Treatments were replicated four times in a randomized complete block design. Fungicide-adjuvant preparations were applied according to guidelines of the Virginia Peanut Leafspot Advisory program<sup>4</sup> using a CO<sub>2</sub>-pressurized sprayer equipped with three D<sub>2</sub>13 (disc-core combination) nozzles per row. Treatments for control of leafspot were applied at 345 kPa and a ground speed of 4.38 km/h, delivering 140 l/ha. Treatments for control of Sclerotinia blight were applied with one 8008LP nozzle centered over each row, delivering 335 l/ha at 165 kPa and a ground speed of 4.38 km/h.

Leafspot incidence and defoliation were assessed every 30 d by visual estimates of the percent of leaflets with one or more spots. Incidence of Sclerotinia blight was evaluated by counts of infection centers in the two center rows of each plot.<sup>10</sup> An infection center was a point of active fungal growth and included 15.24 cm of row length on either side of the point. Yield and quality were determined from the weight of peanuts, adjusted to 7% moisture (w/w). Value was determined by grading a composite sample of peanuts from all four replicates of each treatment in accordance with Federal-State Inspection Service methods.

## III. RESULTS

### A. EFFECT OF SOYOIL 937 ON DROPLET CHARACTERISTICS

The contact angle of water on peanut leaves averaged 127°25', whereas that for paraffin, polypropylene, and polyethylene was 106° 0', 83° 5', and 71° 3', respectively. Paraffin was selected to simulate the peanut leaf in measuring the contact angle of fungicide spray droplets with various levels of adjuvant. The contact angle of droplets with Bravo 720 at 12.5 ml/l of spray volume measured 64° 13' (Table 1). At the same rate of Bravo 720, there was a reduction of contact angle to 56° 25', 53° 0', 50° 38', and 48° 12' as levels of adjuvant increased from 0.5 to 1.0, 2.0, and 4.0% of spray volume, respectively. The contact angle of droplets was transformed to cosine  $\theta$  for regression analysis. The regression equation,  $Y = 0.51286 + 0.0402 X$ , was obtained wherein  $X$  = rate of adjuvant in percent of spray volume and  $Y$  = cosine  $\theta$  of the contact angle. The coefficient of correlation of 0.93 was significant at  $p = 0.05$  (Figure 1). The mean diameter of spray deposits (Bravo 720 at 12.5 ml/l of spray volume) without adjuvant was 255.42  $\mu$ m. There was a positive correlation of size with increasing adjuvant concentration up to 2% SoyOil 937 (Table 2). The size difference between 2 and 4% adjuvant was not statistically significant. The number of droplets per square centimeter decreased as adjuvant concentration increased (Figure 2).

At the same rate of Bravo 720, the distribution of spray droplets without adjuvant approached a Gaussian distribution, with mean and median equal to 253.67 and 222.48  $\mu$ m, respectively (Figure 3A). The distribution pattern shifted toward the larger droplet sizes

TABLE I  
Contact Angle of Spray Droplets  
Containing Bravo 720 and SoyOil 937

SoyOil 937 (% of spray vol) <sup>a</sup>	Contact angle	Cosine $\theta$ <sup>b</sup>
0.0	64° 13'	0.43 d
0.5	56° 25'	0.55 c
1.0	53° 00'	0.60 b
2.0	50° 38'	0.63 ab
4.0	48° 12'	0.67 a

<sup>a</sup> Rates from 0 to 4% of spray volume (140 l/ha) correspond to 0, 0.7, 1.4, 2.8, and 5.6 l/ha of SoyOil 937 with Bravo 720 at 1.75 l/ha.

<sup>b</sup> Contact angles were transformed to cosine  $\theta$  before statistical analysis. Means followed by the same letters are not significantly different at  $p = 0.05$  according to the Waller-Duncan k-ratio procedure.

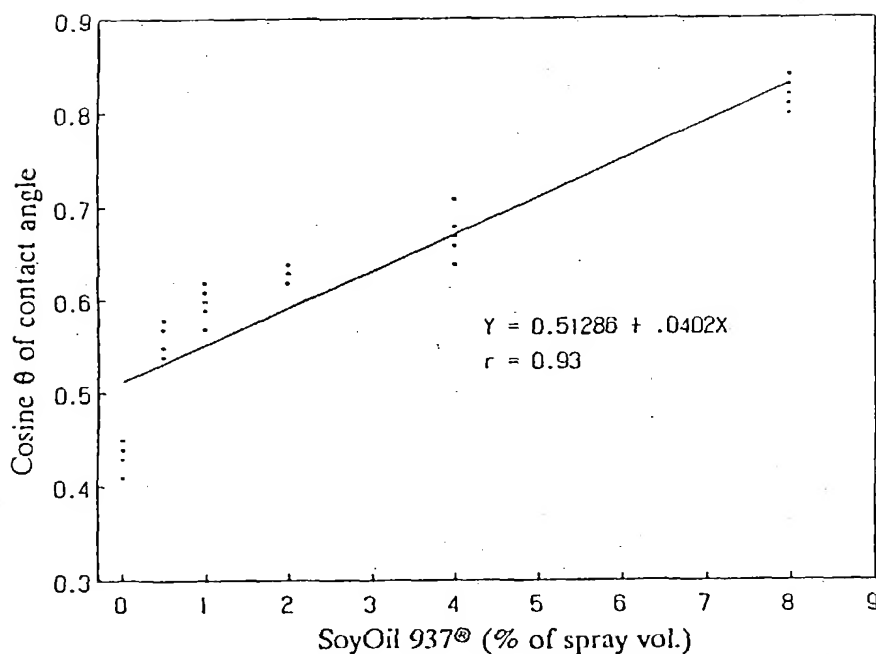


FIGURE 1. Correlation of the cosine  $\theta$  of the contact angle of spray deposits, and adjuvant concentration ( $p = 0.05$ ). Sprays contained Bravo 720 at 1.75 l/ha and SoyOil 937 at 0, 0.5, 1, 2, 4, and 8% of spray volume (140 l/ha).

(Figure 3B and C) as levels of adjuvant were increased from 0 to 1% of spray volume. At 2% of spray volume, droplet size exhibited a distinct bimodal distribution (Figure 3D). There was a shift of the minor mode and major mode positions as well as an increase in droplet size at the 4% level of spray adjuvant (Figure 3E). The mean diameter of droplet deposits increased progressively as adjuvant levels increased from 0 to 2%. Although there was still a numerical increase of median diameter from 2 to 4% adjuvant, the level of increase was not significant.



TABLE 2  
 Characteristics of Spray Droplets with Bravo 720 (1.75 l/ha) and  
 Increasing Levels of SoyOil 937

SoyOil 937 (% of spray vol) <sup>a</sup>	Nozzle discharge (ml/min) <sup>b</sup>	Droplet size ( $\mu$ m) after deposition <sup>c</sup>	Number of droplets per cm <sup>2</sup>	Spray coverage <sup>d</sup> (%)
0.0	351.7 a <sup>e</sup>	255.4 d	197.2 a	10.10 c
0.5	351.7 a	343.0 c	121.4 b	11.22 bc
1.0	355.0 a	407.4 b	98.9 c	12.89 b
2.0	355.0 a	511.6 a	83.5 d	17.16 a
4.0	356.7 a	534.1 a	86.1 d	19.28 a

<sup>a</sup> Based on spray volume of 140 l/ha.

<sup>b</sup> Nozzle discharge was measured at a spray pressure of 345 kPa using a CO<sub>2</sub>-pressurized sprayer with three D<sub>2</sub>L3 (disc-core) nozzles.

<sup>c</sup> Droplets per cm<sup>2</sup> were counted, and the size of 100 droplets was measured after deposition.

<sup>d</sup> Spray coverage was the product of the number of droplets per cm<sup>2</sup> and mean droplet size.

<sup>e</sup> Means in a column followed by the same letters are not significantly different at  $p = 0.05$  according to the Waller-Duncan k-ratio procedure.

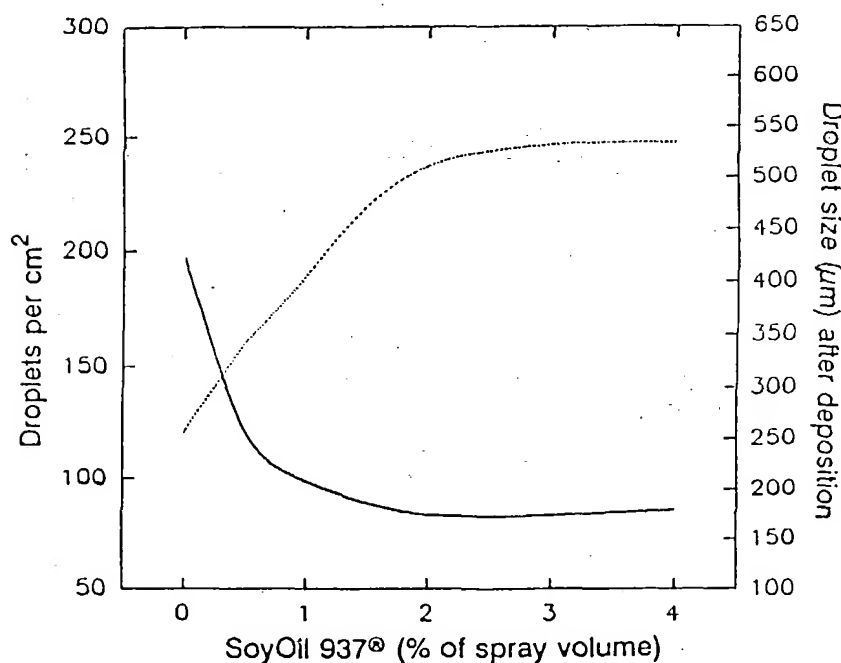


FIGURE 2. Droplet size ( $\mu$ m) after deposition (dotted line) and droplets per square centimeter (solid line) at various levels of SoyOil 937 in percent of spray volume (140 l/ha). Spray contained Bravo 720 at 1.75 l/ha.

## B. FIELD EVALUATION

The evaluation of leafspot incidence during the 2-year period of field studies indicated that SoyOil 937 alone at rates up to 4% of spray volume had no effect on disease. There was a significant reduction of leafspot incidence with application of Bravo 720 alone at rates from 0.44 to 1.75 l/ha. The best level of disease control was obtained with Bravo 720 at 1.75 l/ha and SoyOil 937 at 0.5 to 1.0% of spray volume. Leafspot incidence at the higher

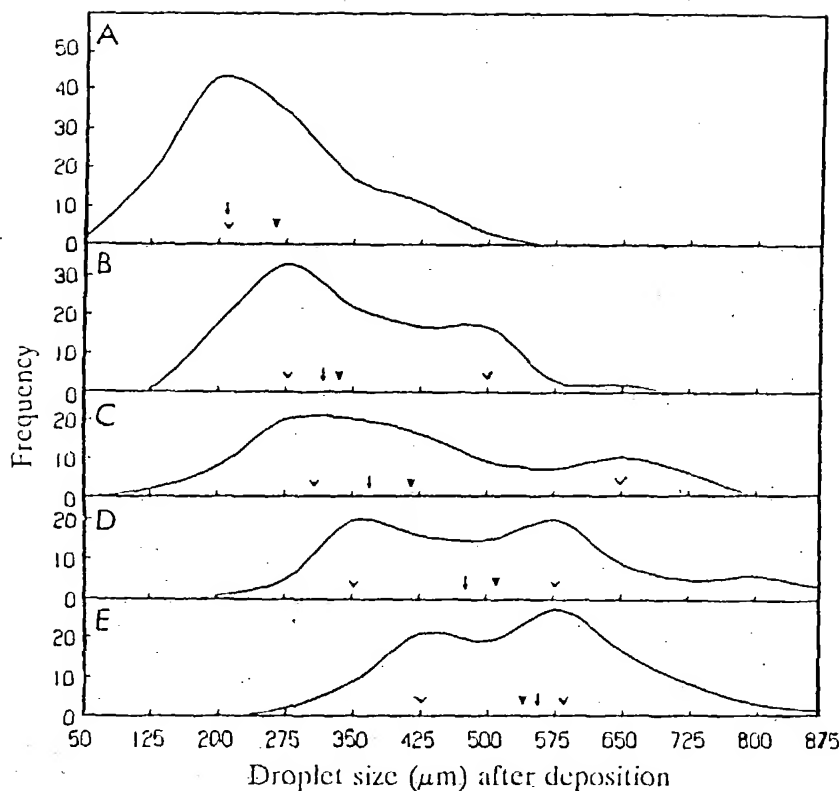


FIGURE 3. Distribution of Bravo 720 with and without SoyOil 937 in various spray categories. (A) Frequency polygon of spray droplets without adjuvant; (B, C) frequency distribution with 0.5 and 1.0% adjuvant, respectively; (D, E) bimodal distribution of droplets with 2 and 4% adjuvant, respectively. (▼ = mean, ↓ = median, v = mode,  $n = 100$ ).

rates of Bravo 720 exhibited a quadratic polynomial curve with increasing levels of adjuvant up to 2% of spray volume. A significant reduction of disease incidence occurred with the 0.5% level of adjuvant, whereas an increase in disease incidence occurred with adjuvant rates exceeding 2% of spray volume (Figure 4).

Yield data from the field study in 1987 did not show a significant improvement by adding SoyOil 937 from 0.5 to 2.0% of spray volume. At the 4% level of adjuvant, there was a significant reduction in yield compared to the treatments without adjuvant at 0.44 and 1.75 l/ha of Bravo 720 (Table 3). The field study in 1988 also showed a reduction in yield at the 4% level of adjuvant compared to almost all of the other treatments. SoyOil 937 did not show any adjuvant effect on the performance of Rovral 50W for control of Sclerotinia blight (Table 4). Disease incidence in plots treated with Rovral 50W showed no significant difference from plots treated with Rovral 50W and adjuvant.

#### IV. DISCUSSION

The degree of water repellency or wettability of leaves largely depends on the composition of cuticular wax and surface roughness.<sup>8</sup> Reducing the surface tension of spray droplets by the use of adjuvant improves the wetting characteristics of spray droplets on waxy surfaces. On the basis of water contact angle, leaves have been classified into two categories.<sup>8</sup> Leaves

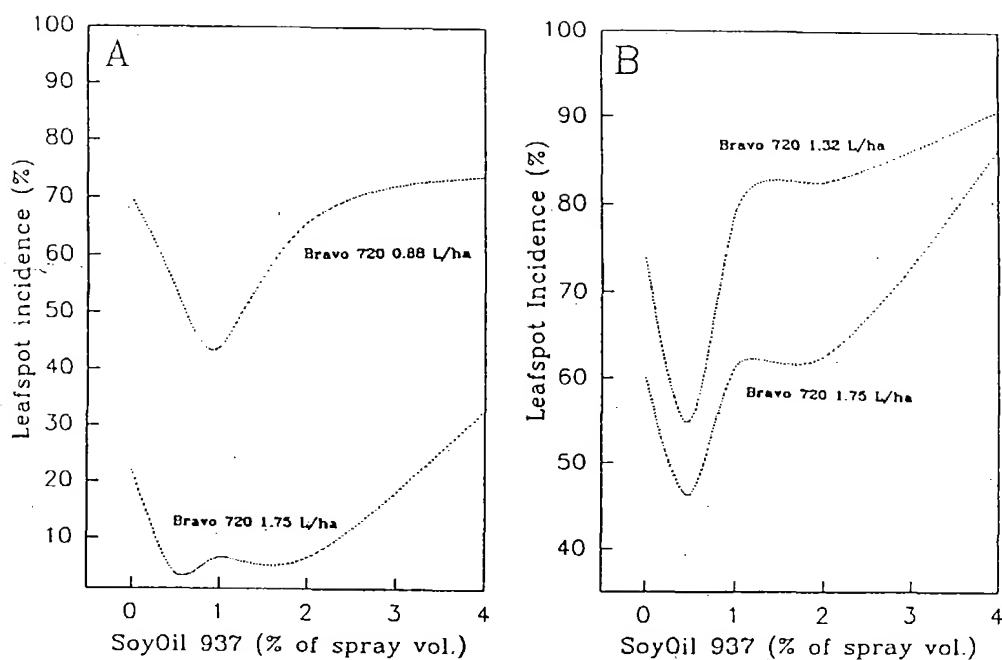


FIGURE 4. Leafspot incidence at various rates of Bravo 720 and SoyOil 937. Graphs A and B are disease incidence data from 1987 and 1988 field tests, respectively.

TABLE 3  
Effect of Bravo 720 With and Without SoyOil 937 on  
Yield of Peanut From Field Trials in 1987 and 1988

SoyOil 937 (% of spray volume)	Bravo 720 (l/ha)				
	0	0.44	0.88	1.32	1.75
1987					
0	4068 g	4957 b-e	4919 c-e	—	5219 a-c
0.5	3993 g	4731 d-f	5056 a-d	—	5307 ab
1.0	3956 g	4831 de	5069 a-d	—	5056 a-d
2.0	4005 g	4882 c-e	4794 de	—	5357 a
4.0	3767 g	4406 f	4668 ef	—	4831 de
1988					
0	3032 c	—	3677 a-c	4219 a	3857 a-c
0.5	—	—	3831 a-c	3909 a-c	4116 ab
1.0	—	—	3780 a-c	3573 a-c	4180 a
2.0	—	—	3922 a-c	3974 ab	4013 ab
4.0	—	—	3470 a-c	3599 a-c	3182 bc

Note: Yield (kg/ha) was determined from the weight of peanuts, adjusted to 7% moisture (w/w). Means with the same letters in a row or column for a given year are not significantly different at  $p = 0.05$  according to the Waller-Duncan k-ratio procedure.

TABLE 4  
Sclerotinia Blight Incidence and Yield of Peanuts  
Following Treatments of Rovral 50W with and  
without SoyOil 937 at 1% of Spray Volume

Fungicide and adjuvant treatment	Disease incidence (hits/plot)	Yield (kg/ha)
Rovral 50W + SoyOil 937	37.5 a	4035 a
Rovral 50W	34.5 a	3884 a
Untreated check	49.0 a	2875 b

Note: Rovral 50W (2.24 kg/ha) was applied at 335 l/ha spray volume. Means in a column are not significantly different at  $p = 0.05$  according to the Waller-Duncan k-ratio procedure.

with a water contact angle  $>90^\circ$  and  $<90^\circ$  were classified as waxy and nonwaxy, respectively. Waxy leaves were further classified into smooth waxy ( $90$  to  $110^\circ$ ) and rough waxy ( $>110^\circ$ ). The peanut leaf having a water contact angle of  $127^\circ 25'$  was, therefore, classified as rough and waxy. SoyOil 937 or other formulations of crop and paraffin-based oil concentrates can be expected to improve wettability by aqueous spray droplets on waxy surfaces.<sup>6</sup>

Linear regression of the cosine  $\theta$  of contact angles for spray mixtures of Bravo 720 and SoyOil 937 indicated a gradual improvement of wettability at increasing levels of adjuvant. The size of droplets after deposition increased with increasing concentrations of adjuvant up to 2% of spray volume. The increase in size resulted in a proportional reduction of droplet density at the same spray discharge volume (Figure 2). Sundaram and Leung<sup>13</sup> also reported a reduction of droplet density and consequent increase of droplet size as spray droplet viscosity was improved with oil. Beyond a level of 2% of SoyOil 937, the change in mean droplet size and droplet density (Table 2) were not significant ( $p = 0.05$ ). The significant change of droplet characteristics below the 2% level of adjuvant and the improvement of surface wettability at increasing levels of adjuvant indicated an optimum adjuvant effect at levels between 0.5 and 1.0% of spray volume.

The dosage-dependent effect of SoyOil 937 at concentrations between 0 and 4% of spray volume was shown by leafspot incidence in field trials. The nonlinear regression curves for leafspot incidence at various levels of adjuvant exhibited quadratic polynomial characteristics, with a significant reduction of disease incidence at an adjuvant level of 0.5% and a significant increase of disease incidence at levels of adjuvant higher than 2% of spray volume. The dosage-dependent phenomenon was observed consistently in 1987 and 1988 field trials with Bravo 720 at rates of 0.88, 1.32, and 1.75 l/ha. This phenomenon might be attributed to an increased level of emulsifier and/or oil on the surface of leaves at high rates of adjuvant. Excessive levels of adjuvant on leaves may increase disease severity in three ways: (1) the emulsifier may dissolve the protective cuticular wax and increase susceptibility of leaves to infection and colonization by pathogens,<sup>7</sup> (2) the emulsifier could enhance the loss of pesticide from wash-off during heavy rain, and (3) the adjuvant may bind tightly or entomb the pesticide, making it unavailable. This is a common phenomenon in pesticide formulations or spray mixtures with high levels of stickers.<sup>15</sup> The first explanation seems unlikely, since application of adjuvant alone did not affect disease severity. The second rationale is the most likely reason for the loss of disease control with Bravo 720 and the 4% level of SoyOil 937. At high rates, the emulsifier may act as a detergent during heavy rain, resulting in the redistribution and wash-off of fungicide from the leaves. This phenomenon is referred to as rewetting.<sup>15</sup>

Bronzing of leaves was observed in plots sprayed with Bravo 720 and high rates of

SoyOil 937. The severity of bronzing increased with increasing concentrations of adjuvant from 1 to 4% of spray volume. At the 1% level of adjuvant with Bravo 720, bronzing was hardly noticeable. Bronzing was not observed in plots sprayed with Bravo 720 or SoyOil 937 alone at various rates.

Yield data did not indicate a significant benefit of adjuvant from 0 to 2% of spray volume with various rates of Bravo 720. At the 4% level of adjuvant, the reduction of disease control was linked to a reduction in yield. The adjuvant effect of SoyOil 937 at 1% of spray volume on iprodione at 2.24 kg/ha was not detected. Both Sclerotinia blight incidence and yield did not reflect significant changes in the performance of iprodione. The nonsignificant differences in this test, however, should not be considered conclusive since rates of Rovral 50W and adjuvant were not varied.

### ACKNOWLEDGMENT

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## Chapter 66

**SPRAY DEPOSITION ENHANCEMENT AND THE CONTROL OF  
*BOTRYTIS* SPP. ON *VICIA FABA* L.**

Christopher F. Green, Helen E. Rimmer, and Deborah A. Green

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## ABSTRACT

Four field experiments were conducted at Prestwold Hall, Noseley Hall, and Saxelby Park in the Midlands of the U.K. Adjuvants known to enhance deposition were admixed with solutions containing the fungitoxics iprodione (Rovral®), vinclozolin (Ronilan®), carbendazim (Stempor®), mancozeb (Penncozeb®), and chlorothalonil (Bravo®). In various fungicide combinations, adjuvants comprising synthetic latex (Bond®), acidified soya lecithin (LI700), pinolines (Nu-Film®, Sprayfast®), and an emulsified mineral oil (Actipron®) were tested.

Only LI700 enhanced the performance of the systemic carbendazim, while Bond was highly effective in increasing the performance of some protectant fungicides in controlling *Botrytis*. However, adjuvant-fungitoxicant interactions were highly specific. Enhancement of dicarboxamide activity by Bond increased the control of *Botrytis* by iprodione, but not by vinclozolin. For fungicides where Bond was highly effective in increasing disease control, LI700 was also effective.

When applied with a proprietary fungicide comprising both iprodione and thiophanate-methyl (Compass®), Bond increased *Botrytis* spp. control, Nu-Film and Sprayfast reduced control, and Actipron had no effect.

## I. INTRODUCTION

Chocolate spot (caused by the fungal pathogens *B. fabae* and *B. cinerea*) is a major cause of yield limitation in crops of *Vicia faba*.<sup>11</sup>

A wide variety of fungitoxics has been used to control *B. fabae* and *B. cinerea* on *V. faba*. The efficacy of systemics has varied, as carbendazim-resistant forms of *B. cinerea* now exist, and protectant products have afforded greater control in more recent experiments.<sup>6,19</sup>

Strong correlations have been reported between chocolate spot infection and yield loss.<sup>7,9</sup> Although Yeoman et al.<sup>19</sup> observed no such relationship, rust (*Uromyces viciae-fabae*) was prevalent in their experiment.

Where disease development continues throughout the season, increasing the number of fungicide applications has improved chocolate spot control and increased yield.<sup>1,6,7</sup> However, where rust and chocolate spot were both present and a second fungicide was applied after the onset of rapid rust development, no further control was afforded, illustrating the importance of application timing.<sup>19</sup>

Bainbridge et al.<sup>1</sup> compared a number of single- and combination-spray timings. The greatest reduction in disease resulted from the latest spray, applied just before disease assessment, although there was little difference in yield between this and an earlier application. Benomyl generally gave the best control of *B. fabae*, although iprodione produced the greatest yield increases, especially when applied early.<sup>1</sup> Decreasing the rate of vinclozolin decreased chocolate spot control and lowered subsequent yield improvements.<sup>9</sup>

Disease prevention through use of fungicides is an important part of management programs for intensive bean production. Inclusion of adjuvants in fungicidal solutions may improve the degree and persistence of *Botrytis* control.

Integrated control strategies should address application timing as well as choice of fungicide and adjuvant. There is a dearth of information concerning the role of spray adjuvants on the control of *Botrytis* on *V. faba*. This chapter attempts to redress that imbalance by examining the influence of selected adjuvants with various fungicides.

## II. MATERIALS AND METHODS

### A. LOCATIONS, HUSBANDRY, AND TREATMENTS

#### 1. Prestwold Hall, 1987

*V. faba* (cv. Bourdon) was sown at 25 seeds per square meter in a clay loam on November 10, 1986; 300 kg ha<sup>-1</sup> K<sub>2</sub>O and 1 t ha<sup>-1</sup> lime were applied prior to sowing. Weed control involved 0.25 kg ha<sup>-1</sup> simazine with 1.4 kg ha<sup>-1</sup> carbetamide on March 4, 1987. *Sitona* was controlled with 30 g ha<sup>-1</sup> fenvalerate on April 30, 1987.

Plots 3 m wide and 20 m long were arranged in three randomized blocks, with fungicide treatments sprayed in 300 l ha<sup>-1</sup> water through 110° fan jet nozzles at a pressure of 1.5 bar. The fungicides applied were (1) 0.550 kg ha<sup>-1</sup> benomyl (Benlate®, DuPont<sup>5</sup>), (2) 0.5 kg ha<sup>-1</sup> iprodione (Rovpal WP®, Rhône-Poulenc<sup>13</sup>), and (3) 0.5 kg ha<sup>-1</sup> vinclozolin (Ronilan®, BASF<sup>15</sup>). All formulations were wettable powders. Fungicide treatments and an untreated control were applied alone, with 1.125 kg ha<sup>-1</sup> soyal lecithin acidified with propionic acid (0.5%, v/v, LI700; Loveland Industries Inc.) or 0.2 kg ha<sup>-1</sup> synthetic latex with a nonionic surfactant (0.14%, v/v, BOND®; Loveland Industries, Inc.) added to the spray solution.

Treatments were applied during early flowering (May 11, 1987), when few *Botrytis* lesions were visible and all were nonaggressive. Untreated guard plots (1.5 m) surrounded each trial plot.

#### 2. Saxelby Park, 1987

On November 2, 1986, 21 seeds of *V. faba* (cv. Bourdon) per square meter were sown into a sandy clay loam. Simazine at 1.15 kg ha<sup>-1</sup> was applied on November 3, 1986, followed by 0.94 kg ha<sup>-1</sup> alloxym-sodium on April 8, 1987 for full spectrum weed control.

Treatments were sprayed during early flowering (May 17, 1987) in 300 l ha<sup>-1</sup> water through 110° fan jet nozzles at 2.0 bar to plots 2 m wide and 10 m long. Applications of (1) 0.5 kg ha<sup>-1</sup> iprodione with 0.5 kg ha<sup>-1</sup> thiophanate-methyl<sup>18</sup> (Compass® Rhône-Poulenc); (2) 0.5 kg ha<sup>-1</sup> carbendazim (Stempor®, ICI<sup>4</sup>); or (3) 1.4 kg ha<sup>-1</sup> mancozeb (Penncozeb, Shell) were tried. Adjuvants comprising synthetic latex (0.14%, v/v, Bond); pinoline (0.1%, v/v, Nu-Film P; 96% poly-1-*p*-menthene, Intracrop®; and 0.1%, v/v, Sprayfast, Mandops); and a 97% emulsified mineral oil (1%, v/v, Actipron, Bayer) were applied in three replicates of completely randomized design (60 plots).

#### 3. Prestwold Hall, 1988

Bourdon faba beans were plowed under into a sandy loam to a depth of 12 ± 4 cm on November 3, 1987. Twenty-nine seeds per square meter were sown following treatments with thiram and thiabendazole. On November 21, 1 kg ha<sup>-1</sup> of carbetamide with 0.5 kg ha<sup>-1</sup> of simazine was applied as a herbicide. On May 10, a complete foliar feed was used (Dow), followed by 0.4 kg ha<sup>-1</sup> daminozide with LI700 on June 5 for developmental manipulation.

Treatments were applied in 220 l ha<sup>-1</sup> water on May 17, 1988, at a pressure of 2.3 bar through 80° fan jet nozzles. Plots 3 m wide and 20 m long were arranged in randomized blocks comprising three replicates of treatments and controls.

Fungicides included (1) 0.5 kg ha<sup>-1</sup> iprodione with 0.5 kg ha<sup>-1</sup> thiophanate-methyl and (2) 1.5 kg ha<sup>-1</sup> chlorothalonil (Bravo 500, BASF). Each fungicide combination and the control (sprayed with water) were treated with or without 0.15 kg ha<sup>-1</sup> synthetic latex with nonionic surfactant (0.15%, v/v, Bond). In addition, thiophanate-methyl was applied with LI700.

#### 4. Noseley Hall, 1988

On October 30, 1987, 25 seeds of *V. faba* (cv. Bourdon) per square meter were sown

into a heavy clay. Immediately after sowing, 1.0 kg carbetamide with 1.0 kg simazine was applied, which provided good weed control throughout the season. Treatments comprised Compass applied at 0, 0.5, 1.0, 2.0, and 3.0 l ha<sup>-1</sup>, equivalent to 0, 0.084, 0.17, 0.33, and 0.5 kg ha<sup>-1</sup> of both iprodione and thiophanate-methyl, with or without Bond at a 0.14% (v/v) dilution in the spray solution.

Plots measured 3 m wide and 10 m long, and were arranged in two randomized blocks.

## B. OBSERVATIONS AND MEASUREMENTS

Twenty leaves (two from the podding region on each of ten plants) per plot were randomly selected and arranged under a polythene sheet superimposing 400 random dots. The frequency of spots intersecting with chocolate spot lesions as a proportion of the total overlying leaf tissue was used as an estimate of infection. Treatment means were based on untransformed data. A logit transformation of percentages (P%),  $0.5 \ln (0.05 + P\%)/(100.05 - P\%)$  was used for analysis of variance.

When full maturity was reached at all sites except Noseley Hall, two separate 1-m<sup>2</sup> quadrats were removed from the center of each plot. These were used to determine yield and yield components. Plants were dried in a ventilated oven at  $80 \pm 5^\circ\text{C}$  for 48 h.

## III. RESULTS AND DISCUSSION

### A. BOTRYTIS INFECTION AND CONTROL

#### 1. Model

Sequential observations of foliar infection allowed an analysis of fungitoxicant/adjuvant effects on pathogen population expansion, using necrotic lesions as a surrogate indicator of pathogen magnitude. To characterize the time course of such an event by three simple parameters, we propose to use a simple bilinear interpolation:

$$\beta = \begin{cases} \xi(t - t_i) & t_{\max} \gg t \gg t_e \\ \beta_{\max} - \varphi(t - t_m) & t > t_m \end{cases} \quad (1a)$$

$$(1b)$$

where  $\beta$  is the infection by *Botrytis* (percentage of foliage covered by necrotic lesions),  $\xi$  is the rate of increase in  $\beta$  with time ( $t$ ) at the time when the infection is rapidly expanding after a time,  $t_e$ .  $\beta$  may peak ( $\beta_{\max}$ ) at a time  $t_m$ , after which the relationship may take on a parabolic ( $\varphi > 0$ ) or asymptotic ( $\varphi = 0$ ) form.

On the  $t$  axis,  $t_i$  is the point where it would be crossed by an extrapolation of a linear regression of  $\beta$  upon  $t$  when  $t_m \geq t \geq t_e$  (i.e.,  $t_i = t_m - [\beta_{\max}/\xi]$ ), and is thus directly indicative of the length of time before "aggressive" expansion of the *Botrytis* infection became evident.

Fungicide/adjuvant efficacy can be assessed by changes in the duration to acceleration of aggressive infection ( $t_i$ ), the rate of infection throughout the aggressive expansion ( $\xi$ ), and the maximum level of infection recorded ( $\beta_{\max}$ ). Sequential observations of the foliage failed to determine the nature of the infection beyond  $\beta_{\max}$ . However, Figure 1 suggests that an asymptote may have been reached by  $t_m$ .

#### 2. Prestwold Hall, 1987

Spraying coincided with <1% nonaggressive lesions on the leaf tissue (Figure 1). Equation 1a fitted the data closely ( $0.2 > p > 0.002$ ). In untreated plots, rapid expansion of infection began around 20 d after spraying (Table 1, Figure 1). This was delayed by only

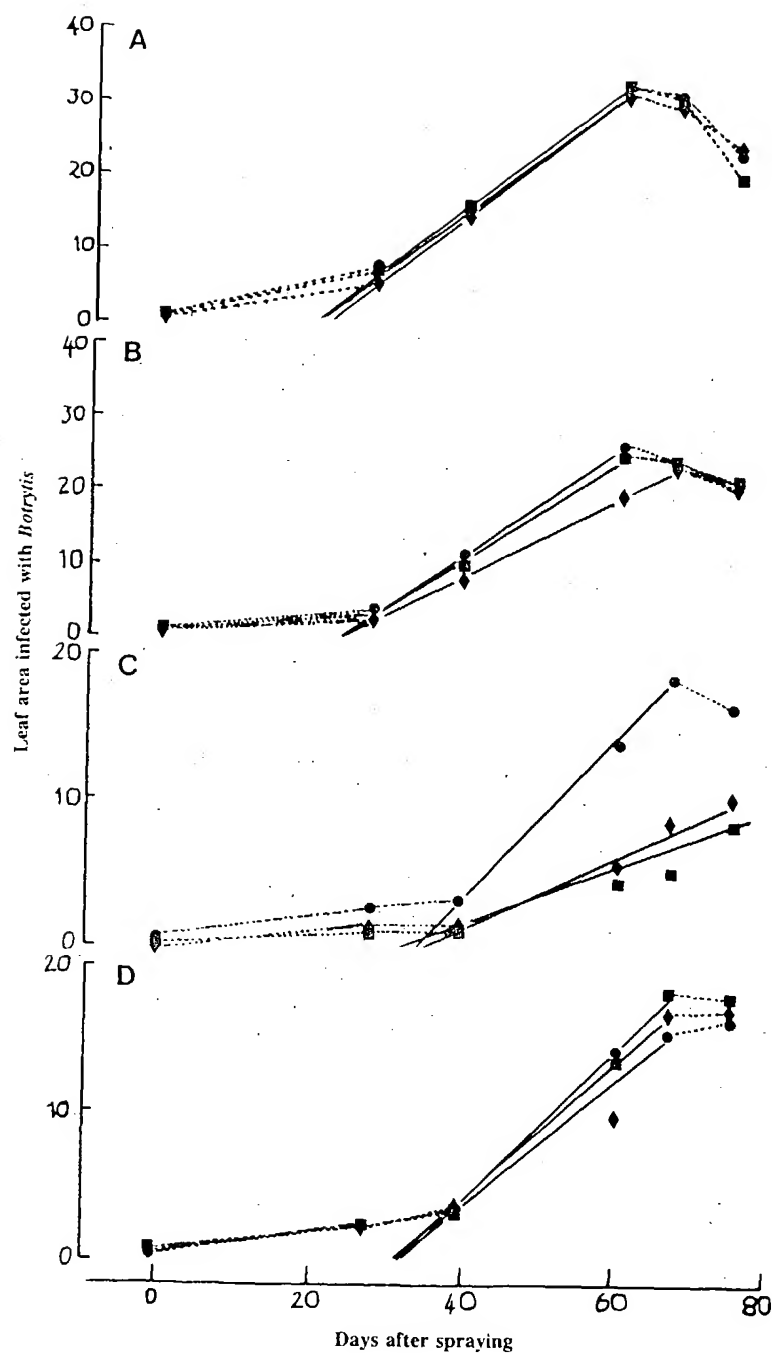


FIGURE 1. Time course of *Botrytis* infection on *V. faba* at Prestwold in 1987 fitted by least-squares regression during the linear phase (—). (A) Untreated, (B) benomyl, (C) iprodione, and (D) vinclozolin, without adjuvant (●) or with LI700 (◆) or Bond (■) added to the spray solution.



TABLE 1  
Parameters in the Relationship Between the Infection of Foliage by *Botrytis* spp. ( $\beta$ ) and Days Postfungicide Application for Prestwold Hall, 1987

Treatment	Adjuvant	$t_i$ (days postspraying)	$t_m$ (days postspraying)	$\beta_{max}$ (%)	$\xi$ ( $\pm$ SE) (% d <sup>-1</sup> )	R <sup>2</sup>	p
None	None	17	60	33	0.76 (0.021)	0.998	0.917
None	LI700	20	60	32	0.80 (0.003)	>0.999	0.002
None	Bond	18	61	33	0.77 (0.043)	0.994	0.036
Benomyl	None	23	61	27	0.72 (0.051)	0.990	0.045
Benomyl	LI700	23	68	24	0.53 (0.028)	0.994	0.034
Benomyl	Bond	23	60	25	0.68 (0.028)	0.997	0.026
Iprodione	None	33	68	19	0.54 (0.029)	0.994	0.034
Iprodione	LI700	35	77	10	0.24 (0.055)	0.897	0.146
Iprodione	Bond	30	*	7	0.11 (0.057)	0.693	0.108
Vinclozolin	None	31	66	16	0.46 (0.068)	0.958	0.093
Vinclozolin	LI700	32	72	17	0.43 (0.140)	0.811	0.199
Vinclozolin	Bond	33	67	18	0.53 (0.032)	0.993	0.039

3 d using benomyl and by nearly 2 weeks using the dicarboximides, vinclozolin and iprodione. Adjuvants, when admixed with the spray solution, had little effect on  $t_i$ , but significantly ( $p < 0.05$  on comparison of regression slopes<sup>16</sup>) reduced  $\xi$ . As  $t_m$  was little affected by treatment,  $\beta_{max}$  was reduced in proportion to the reduction in  $\xi$  ( $\beta_{max} = 39.6 [\pm 1.12 \text{ SE}] \xi$ ,  $R^2 = (0.991, p < 0.0001)$ ).

Adjuvants LI700 and Bond applied alone had no significant ( $p > 0.2$ ) effect on *Botrytis* infection at any time during the period of measurement. Without adjuvants, the wettable powder formulations of iprodione and vinclozolin proved equally effective in preventing *Botrytis*, while benomyl provided useful early suppression (about 60% control), which declined rapidly to 10% by mid-July. Synthetic latex (Bond) failed ( $p > 0.2$ ) to influence the control afforded by the benzimidazole fungicide, while LI700 significantly ( $p < 0.1$ ) increased control during the middle of disease expansion when benomyl's apparent effectiveness was declining, eventually doubling the control by July 10, 1987 (Figure 2).

During June, applying either dicarboxamide without adjuvants gave >70% control, but during July, persistence of the effect was inadequate and control dropped to 30%. Both LI700 and Bond had no influence on the control of *Botrytis* by vinclozolin (Table 1, Figure 1D).

In stark contrast, both adjuvants enhanced the control of *Botrytis* by iprodione, evidencing the complex nature of adjuvant/fungitoxicant specificity (Figure 2). LI700 reduced  $\xi$  to around half of that given by iprodione (which individually reduced the control  $\xi$  by almost one third). Bond was slightly more effective, reducing the rate of disease infestation to 24% of the untreated control and to 20% of the rate in the presence of an iprodione spray alone.

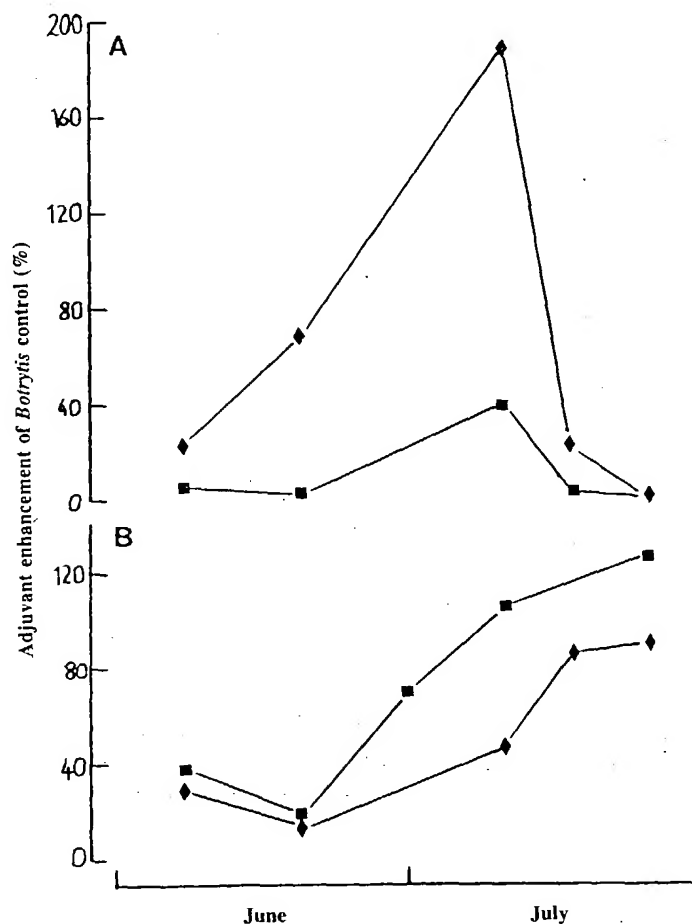


FIGURE 2. Percentage increase in control of *Botrytis* on *V. faba* at Prestwold 1987 following addition of LI700 (◆) or Bond (■) to (A) benomyl or (B) iprodione.

In short, adding synthetic latex as a deposition agent provided a greater advance in *Botrytis* control than adding an iprodione spray alone. Similarly, while vinclozolin (with and without adjuvants) and iprodione (without adjuvant) almost halved  $\beta_{max}$ , iprodione/LI700 and iprodione/Bond reduced  $\beta_{max}$  by over two thirds (Table 1, Figure 1).

In practice, selecting between two dicarboxamides is superficially unimportant, considering the merits of the fungicides alone. An increase in efficacy followed inclusion of adjuvant with iprodione alone, changed the emphasis of dicarboxamide selection. Adding Bond to iprodione increased control such that, in commercial practice, a second spray application would have been unnecessary, with obvious gross margin and perceived environmental advantages.

### 3. Saxelby Park, 1987

At Saxelby, *Botrytis* infection was severe, as untreated canopies reached 47% of foliage covered with necrotic lesions by mid-July. However, fungicides were applied when <2% infection was present.

Yeoman et al.<sup>19</sup> reported some suppression of *Botrytis* on *V. faba* (cv. Minden) using ethylene-bis dithiocarbamates. Improved control of *Phytophthora infestans* on *Solanum tub-*

TABLE 2  
Infection by *Botrytis* spp. on *V. faba* at Saxelby Park in 1987 Following  
Fungicide Application with Various Spray Adjuvants

Fungicide	Adjuvant	% <i>Botrytis</i> infection		Seed yield (t ha <sup>-1</sup> @ 85% DM)
		June 19	July 17	
None	None	19.6	47.4	3.26
Thiophanate-methyl/iprodione	None	4.4	20.3	4.23
Thiophanate-methyl/iprodione	Bond	1.4	5.7	4.71
Thiophanate-methyl/iprodione	Nu-Film P	14.3	31.2	3.69
Thiophanate-methyl/iprodione	Sprayfast	15.8	33.0	3.67
Thiophanate-methyl/iprodione	Actipron	8.9	19.2	4.14
Carbendazim	None	13.4	38.6	3.62
Carbendazim	Bond	12.2	38.8	3.99
Carbendazim	NufilmP	16.0	36.3	3.73
Carbendazim	Sprayfast	15.7	44.0	3.33
Carbendazim	Actipron	14.7	30.6	4.32
Mancozeb	None	20.1	49.3	3.19
Mancozeb	Bond	11.0	40.1	3.79
Mancozeb	Nu-Film P	15.1	45.4	3.34
Mancozeb	Sprayfast	14.8	42.5	3.29
Mancozeb	Actipron	22.9	42.5	3.30
SE		1.96	4.03	0.225
P		<0.001	<0.001	<0.0001

*erosum* resulted from using Bond as a sticker for mancozeb.<sup>17</sup> In this field experiment, mancozeb gave an early suppression of *Botrytis*, an effect that was lost by mid-July (Table 2). Better control was effected using carbendazim or mancozeb with Bond. However, by mid-July, MBC-treated plots had levels of *Botrytis* not significantly different ( $p > 0.2$ ) from the control.

An oil-based formulation of the benzimidazole generator, thiophanate-methyl with iprodione in equal proportion, provided excellent *Botrytis* control. Early control and the rate of disease development were reduced by thiophanate-methyl with iprodione. Adding Bond reduced the initial infection to one fourth of that of thiophanate-methyl with iprodione alone, an effect that persisted late in the epidemic. Additional mineral oil (Actipron) did not affect control. The terpene-based stickers Nu-Film P and Sprayfast reduced the effect of thiophanate-methyl with iprodione initially to a level not significantly different from the control. Later (July 17), the fungicide/terpene treatments provided marginal control of *Botrytis*, but levels of infection in these treatments were >30% (Table 2), probably due to the large inoculum source as a consequence of poor early control.<sup>10</sup>

#### 4. Prestwold Hall, 1988

Spraying coincided with 3.8 ( $\pm 0.32$  SE) nodes per plant in flower and 67.6 ( $\pm 3.61$  SE)% ground cover. Measurements on spray transmitted to petri dishes placed at the base of the canopy (two per plot) inferred an 85 ( $\pm 3.2$  SE)% retention of spray. During early and mid-flowering (up to 2 weeks postspraying), *Botrytis* remained nonaggressive, and the foliar lesions covered only 1% of the foliage. All treatments failed to affect necrotic pathogen damage during early infection (Figure 3).

Thirty-four days after spraying *Botrytis* infection in the untreated stand reached 9%, giving scope for control by fungicide/adjuvant combinations. Equation 1a gave  $\xi$  between 0.1 and 0.32% d<sup>-1</sup>. While chlorothalonil reduced development by 25%, Bond did not enhance the performance of this fungicide. Thiophanate-methyl with iprodione applied alone provided control equal to chlorothalonil and chlorothalonil/Bond mixtures (Table 3, Figure

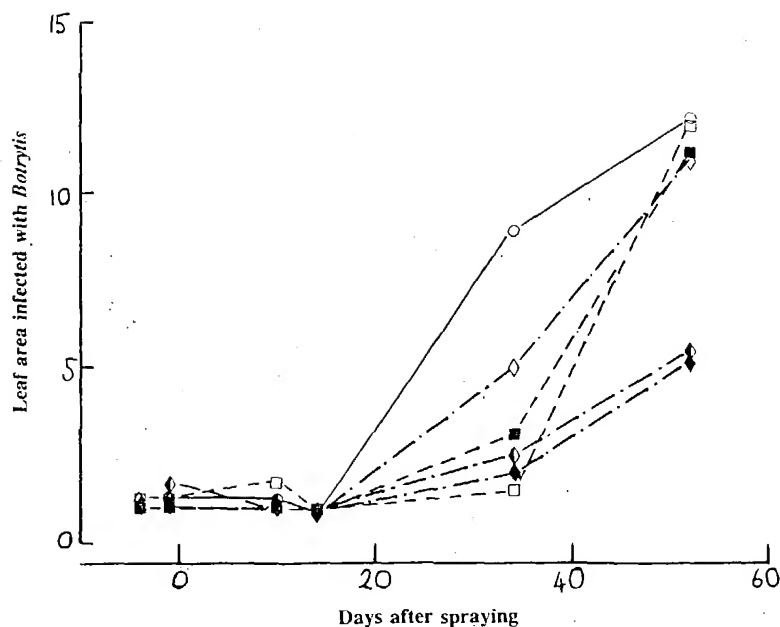


FIGURE 3. Time course of *Botrytis* infection of *V. faba* at Prestwold in 1988 treated with chlorothalonil ( $\square$ ,  $\blacksquare$ , —) or thiophanate-methyl/iprodione ( $\diamond$ ,  $\blacklozenge$ ,  $\diamond$ , - - -) with Bond (closed symbols), LI700 ( $\diamond$ ), no adjuvant (open symbols), or compared with an untreated control ( $\circ$  —).

3). Only thiophanate-methyl with iprodione applied with LI700, and especially with Bond, significantly reduced  $\xi$  (53 and 70%, respectively; Table 3) and  $\beta_{\max}$  ( $p = 0.01$ , Figure 3).

#### 5. Noseley Hall, 1988

Figure 4 gives dose rate/response curves of *Botrytis* infection to thiophanate-methyl with iprodione 30 d after spraying. At full application rates ( $0.5 \text{ kg ha}^{-1}$  of both iprodione and thiophanate-methyl), 80% control resulted and was unaffected by adding Bond to the spray solution. Describing the data by exponential (without Bond) or by linear power (with Bond) functions (see legend to Figure 4), the increase in performance due to adjuvant is dependent upon dose rate. Where rates are adequate for good control without adjuvant, potential improvements in deposition have no effect. A similar situation is evident at grossly sub-optimal rates. However, where the doses used are adequate for control, i.e., if adjuvants ensure that deposition is even and fungicides remain on the foliage, large increases in disease control are possible (Figure 4). The equations in Figure 4 suggest that thiophanate-methyl with iprodione at less than two thirds of the recommended rate plus Bond gave disease control equivalent to the recommended rate of the fungicide combination alone.

#### B. SEED YIELD

Where *Botrytis* infection occurred late in the season, seed yield was not affected by control (Prestwold Hall, 1988). At Prestwold Hall in 1987, seed yield ( $\gamma$ , Table 4) was closely related to *Botrytis* infection, as characterized by the rate of disease development ( $\xi$ ):

$$\gamma_s = 7.42(\pm 0.17 \text{ SE}) - 2.21(\pm 0.29 \text{ SE}) \xi \quad (2)$$

with  $R^2 = 0.84$  and  $p < 0.0001$ , and  $\gamma_s$  in units of  $\text{t ha}^{-1}$ . This suggests that for every 1% increase in  $\beta_{\max}$  (dependent upon  $\xi$ ), yield will be lost at  $56 \text{ kg ha}^{-1}$  or 0.75%.

TABLE 3  
Yield, Yield Components, and Mean Rate of *Botrytis* spp. Population Growth ( $\xi$ ) on Leaves of *V. faba* at Prestwold Hall in 1988

Fungicide	Adjuvant	Seed yield (t ha <sup>-1</sup> @ 85% DM)	Biomass (t ha <sup>-1</sup> )	Harvest index (%)	$\xi$ ( $\pm$ SE) (% d <sup>-1</sup> )	R <sup>2</sup>
None	None	9.3	14.6	52	0.32 (0.046)	0.98
Chlorothalonil	None	12.5	20.2	51	0.24 (0.107)	0.83
Chlorothalonil	Bond	8.3	13.8	49	0.24 (0.065)	0.93
Thiophanate-methyl/iprodisone	None	8.9	15.1	49	0.26 (0.024)	0.99
Thiophanate-methyl/iprodisone	Bond	8.7	14.6	50	0.10 (0.023)	0.95
Thiophanate-methyl/iprodisone	LI700	11.6	18.0	53	0.15 (0.016)	0.98
SE		3.35	4.43	4.60	—	—
<i>p</i>		0.63	0.47	0.81	—	—

Similarly, at Saxelby Park in 1987,  $\gamma_s$  was directly related to the weighted mean of *Botrytis* assessments ( $\bar{\beta}$ ):

$$\gamma_s = 4.93(\pm 0.15 \text{ SE}) - 0.05(\pm 0.01 \text{ SE}) \bar{\beta} \quad (3)$$

with  $R^2 = 0.82$  and  $p < 0.0001$ , i.e., a 1% drop in yield for every 1% increase in the mean level of *Botrytis* infection.

#### IV. CONCLUSIONS

Data recorded in the four field trials presented above suggest specificity in the relationship between adjuvants and fungitoxics. While Bond and LI700 increased *Botrytis* control on *Vicia* using one dicarboxamide (iprodisone), no effect was observed with another dicarboxamide (vinclozolin). Further, while the dicarboxamide-benzimidazole formulation (Compass) showed improved suppression of *Botrytis* development if a synthetic latex adjuvant (Bond) was added, Actipron had no effect and the pinolines, Nu-Film P and Sprayfast, actually reduced control. The possibility of fungicide encapsulation, i.e., solubilization into leaf material that may be a barrier to activity or conversion to nontoxicant metabolites, must be studied. In any event, adjuvant mixtures with fungicides, while showing great potential for disease control, must be embraced with caution and only undertaken on objective grounds from clear experimental evidence.

Bond showed consistent benefits to *Botrytis* control with iprodisone-based Rovral and Compass. Prophylactic applications of iprodisone-Bond reduced the rate of early disease development better than other fungicide-adjuvant combinations (Figures 1, 2, and 4; Tables 1 and 2). At Prestwold in 1988, where *Botrytis* did not develop until late in ontogeny, only sprays containing iprodisone with thiophanate-methyl and Bond persisted to ensure late-season control.



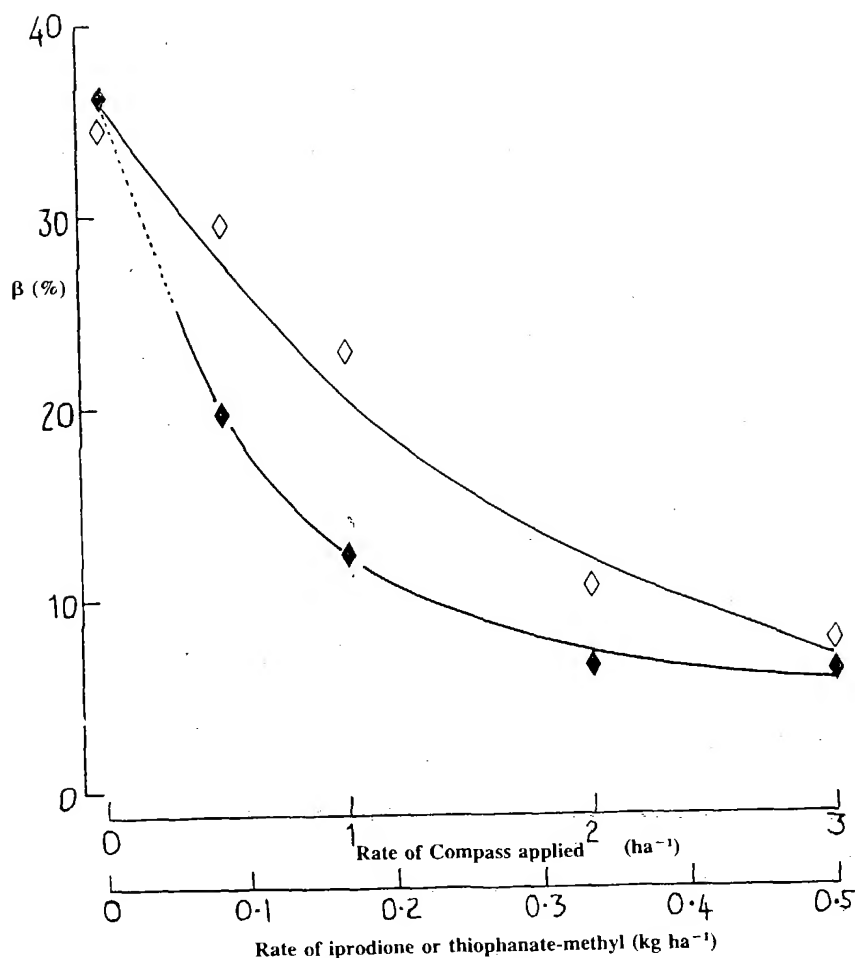


FIGURE 4. Decline in *Botrytis* spp. infection at Nosceley Hall in 1988 as the rate of thiophanate-methyl/iprodione is increased with (◆) or without (◇) Bond added to the spray solution as an adjuvant. Fitted lines (—) for without Bond are described by an exponential equation:

$$\beta = 33.6 (\pm 1.09 \text{ SE}) \exp[-0.55 (\pm 0.055 \text{ SE}) \text{ dose rate}]; R^2 = 0.97, p = 0.002$$

or with Bond by a linear power equation:

$$\beta = 12.01 (\pm 1.06 \text{ SE}) \text{ dose rate}^{-0.708 (\pm 0.079 \text{ SE})}; R^2 = 0.96, p = 0.012$$

Studies have shown that Bond acts by binding active ingredients in a surface latex film.<sup>17</sup> (Reeves, personal communication 1987). Dicarboxamides mainly inhibit mycelial growth, and a retained concentration on the surface in a latex film has obvious advantages in this respect.<sup>2,3,8,14</sup> For LI700, the influence of soyal lecithin on deposition and surface solubilization is less clear. Any increase in solubility could be an advantage, as dicarboxamides have shown limited migration within plant tissues.<sup>12</sup> Postulation and interpretation of this kind, however, does nothing to explain the poor responses of vinclozolin to mixtures with both LI700 and Bond, which may be a function of vinclozolin chemistry or the Ronilan formulation.

TABLE 4  
Yield and Yield Components of *V. faba* Infected with *Botrytis* at Prestwold Hall in 1987

Treatment	Adjuvant	Yield (DM) (t ha <sup>-1</sup> )	Plants (m <sup>-2</sup> )	Branches per plant	Podded nodes per branch	Pods per node	Mean seed weight (g)	% Increase in seed yield	Seeds per pod
None	None	5.62	18.0	1.24	9.63	1.97	0.41	—	3.27
None	L1700	5.73	18.0	1.32	9.50	2.07	0.38	2.0	3.27
None	Bond	5.60	17.7	1.25	9.47	2.01	0.41	0	3.30
Benomyl	None	5.86	17.7	1.33	9.50	2.41	0.34	4.3	3.30
Benomyl	L1700	5.97	17.7	1.32	9.43	2.20	0.39	6.2	3.20
Benomyl	Bond	5.90	17.7	1.32	9.30	2.37	0.37	5.0	3.13
Iprodione	None	6.75	18.3	1.30	9.53	2.22	0.42	20.1	3.23
Iprodione	L1700	6.87	18.0	1.29	9.33	2.35	0.41	22.2	3.27
Iprodione	Bond	7.15	17.3	1.31	9.40	2.39	0.45	27.2	3.17
Vinclozolin	None	6.27	18.0	1.30	9.53	2.22	0.39	11.6	3.27
Vinclozolin	L1700	6.44	17.7	1.34	9.53	2.24	0.39	14.6	3.27
Vinclozolin	Bond	6.41	18.3	1.29	9.47	2.23	0.39	14.1	3.30
SE		0.157	1.24	0.07	0.46	0.21	0.04	—	0.08

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## Chapter 67

EFFECTIVENESS OF BACULOVIRUSES AS INFLUENCED BY  
DIFFERENT ADDITIVES

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## I. INTRODUCTION

It has been well documented that the use of broad-spectrum, persistent chemical insecticides has created several problems such as environmental pollution, pest resurgence, residues in food and water, and development of resistance in insects. There is an urgent need to develop specific and safe alternative pest control methods. Microbial insecticides have many characteristics ideally suited for use in pest management programs. They are usually specific and highly virulent on a given host, pose little hazard to nontarget organisms, and are usually compatible with other management programs.

For short-term control, viruses are commonly applied as suspensions in water-base spray formulations or emulsifiable suspensions, wettable powders, dusts, baits, and granules. Numerous factors are considered in developing efficient and safe spray formulations with regard for biological and physicochemical properties. Most formulations contain various additives such as wetting agents and spreaders, adhesives or stickers, viscosity control agents, antitracers for spray deposit assessment, and other ingredients.

The most recent research in microbial control of baculoviruses has been directed toward developing methods for increasing the dependability and effectiveness of the nuclear polyhedrosis virus. As the ultra-violet (UV) rays of sunlight are known to impair the biological activity of the virus, use of sunlight protectants in spray formulations has been advocated. Many substances have been tested for their capacity to shield baculoviruses against UV rays, and some have been included in commercial preparations. The most successful substances have been various forms of carbon. The most finely divided preparations appear to give the best results, e.g., activated charcoal and Indian ink. In combination with a sticker, e.g., egg albumen or skimmed milk, which itself may confer some protection, good persistence has been achieved. Many attempts have been made to enhance the uptake of baculoviruses by insect pests, and these have been especially associated with *Heliothis* on cotton — because of the economic importance of cotton and the inconsistent performance of nuclear polyhedrosis viruses (NPVs) applied as sprays to that crop.<sup>6</sup> The use of feeding stimulants in combination with the virus to increase ingestion by the target pest is another way to improve the formulation.<sup>3</sup>

*H. armigera*, commonly known as gram pod borer, is a serious pest of pulses, cotton, sorghum, and sunflower in the Marathwada region of India. The NPV isolated by Waghmare<sup>17</sup> has been extensively studied.<sup>1,10-15</sup>

The Bihar hairy caterpillar, *Spilosoma (Diacrisia) obliqua* is a polyphagous pest, assuming serious proportions during certain years, especially on crops like sunflower, castor, green gram, and black gram. *S. obliqua* is difficult to control with chemical pesticides, particularly in its advanced stage of development. The NPV of this pest was isolated in larvae collected from sunflower fields. Preliminary field evaluation studies revealed its potential for development as a microbial pesticide.<sup>2</sup>

This chapter presents the results of laboratory and field studies undertaken to evaluate the efficacy of the NPVs of the American bollworm, *Heliothis armigera*, and Bihar hairy caterpillar, *Spilosoma (Diacrisia) obliqua*, as influenced by the different additives.

## II. MATERIALS AND METHODS

### A. LABORATORY STUDIES

#### 1. Maintenance of Healthy Cultures

Disease-free cultures of *H. armigera* and *S. obliqua* were raised from nucleus cultures obtained from sunflower fields. For maintaining the culture of *H. armigera*, larvae were reared on a semisynthetic diet, while *S. obliqua* larvae were reared on fresh sunflower leaves.



## 2. Virus Stocks

The inoculum of *H. armigera* NPV was a sample of the original isolate from *H. armigera* on pigeonpea. Similarly, the inoculum of *S. obliqua* NPV was a sample of the isolate from *S. obliqua* on sunflower. Both these isolates are maintained at the Microbial Control Laboratory of the Department of Entomology, Marathwada Agricultural University, Parbhani. The virus suspensions were purified by differential centrifugation, and the counts of polyhedral inclusion bodies (PIBs) were made using an improved Neubaur Haemocytometer. The stock suspensions were diluted with sterile distilled water to give  $4 \times 10^7$  PIBs/ml for *H. armigera* NPV and  $1 \times 10^6$  PIBs/ml for *S. obliqua* NPV, as these concentrations in earlier studies were determined to be the  $LC_{50}$  values for the respective insect hosts.

## 3. Bioassay with Adjuvants

The adjuvants tested were cottonseed meal at 5 and 10%, egg albumen at 0.3%, jaggery at 5%, Tinopal at 0.01%, and soybean flour at 5 and 10% in various combinations.

Third-instar larvae of *H. armigera* and *S. obliqua* were starved for 4 h. The sunflower leaves were dipped in various combinations of the adjuvants and virus, and dried under a fan before feeding. Three replications of 20 larvae each were kept for all treatments, including a control. Larvae of *H. armigera* were kept singly in plastic containers (5 by 4 cm). *S. obliqua* larvae were kept in 15 by 2.5-cm petri dishes in groups of 20 each. The larvae were allowed to feed on treated leaves for 24 h, then reared on fresh food until death or pupation at  $27 \pm 1^\circ\text{C}$  in a BOD incubator. Suitable controls were maintained without virus treatments. Mortality was recorded daily, and the cadavers checked for the presence of PIBs. Data on the percentage of mortality were converted to angles for analysis of variance, using a complete randomized block design, and the means were analyzed by Duncan's multiple range test.<sup>5</sup>  $LT_{50}$  values were calculated using the formula suggested by Biever and Hostetter.<sup>4</sup>

## B. FIELD STUDIES

Field trials were conducted to evaluate the efficacy of *Heliothis* NPV, as influenced by different additives, against *H. armigera* on pigeonpea and chickpea. The experiments were laid out in randomized block design using the ICPL-87 variety of pigeonpea and Chafa variety of chickpea at the Main Research Farm, College of Agriculture, Marathwada Agricultural University, Parbhani, during the Kharif and Rabi seasons of 1987 and 1988, respectively. In all, ten treatments were replicated three and four times for pigeonpea and chickpea, respectively. The gross and net plot sizes were 10.80 and 6.48 m<sup>2</sup> for pigeonpea and 9.0 and 6.72 m<sup>2</sup> for chickpea. Pigeonpea was sown on July 3, 1987, and chickpea on October 28, 1987. Two rounds of treatments were given. For pigeonpea, the first spraying of NPV at 250 l/ha + additives was carried out on October 1, 1987, when the crop was in the initial flowering stage and the early instars of *H. armigera* were seen. The second spray was carried out 2 weeks later. For chickpea, the first spraying was done on December 19, 1987, when the crop was in the flowering stage and the incidence of *H. armigera* was noticed. The second spraying was undertaken 3 weeks later (January 12, 1988), when the crop was in the pod-formation stage. A backpack knapsack sprayer with NMD 6564 nozzles was used for spraying at 500 l/ha. All sprays were applied during evening hours.

The effectiveness of different treatments was judged on the basis of larval mortality, pod damage at harvest, and grain yield. Thirty medium-size (third to fourth instar) larvae were collected 2 d after each spraying from all replications of a given treatment involving pigeonpea, and 20 larvae from each treatment on chickpea. The larvae were reared individually and mortality was recorded daily until death or pupation. Data on larval mortality, pod damage, and yield were subjected to statistical analysis.<sup>4,5</sup>

In another experiment, the field persistence of *Heliothis* NPV with selected additives

TABLE I  
Effect of Different Additives and NPV on Mortality of Third Instar *Heliothis armigera* and *Spilosoma obliqua*

Treatment* (% wt in water)	<i>H. armigera</i>		<i>S. obliqua</i>	
	Mean % mortality	LT <sub>50</sub> (h)	Mean % mortality	LT <sub>50</sub> (h)
NPV	60.0 b	204	40.0 d	—
NPV + cotton seed meal (5%)	70.0 ab	192	63.3 a-c	256
NPV + cotton seed meal (10%)	65.0 b	200	60.0 a-c	256
NPV + egg albumen (0.3%) + Tinopal (0.01%)	80.0 ab	174	66.7 ab	247
NPV + egg albumen (0.3%) + Tinopal (0.01%) + jaggery (5%)	70.0 ab	192	60.0 a-c	255
NPV + egg albumen (0.3%) + Tinopal (0.01%) + cotton seed meal (5%)	65.0 b	186	58.3 bc	258
NPV + soybean flour (5%)	70.0 ab	192	53.3 c	261
NPV + soybean flour (10%)	75.0 ab	198	60.0 a-c	256
NPV + egg albumen (0.3%) + Tinopal (0.01%) + soybean flour (5%)	85.0 a	180	68.3 ab	246
NPV + egg albumen (0.3%) + Tinopal (0.01%) + soybean flour (5%) + jaggery (5%)	85.0 a	174	70.0 a	247
Untreated control	0.0 c	—	0.0 e	—
SEM	3.952		1.849	

Note: Means followed by the same letter in a column are not significantly different at  $p = 0.05$ .

\* *Heliothis* NPV,  $4 \times 10^7$  PIBs/ml; *S. obliqua* NPV,  $1 \times 10^6$  PIBs/ml.

was evaluated on a field of sunflowers sown at a spacing of 45 by 15 cm on June 23, 1988. Nine plots, 1.8 by 3.0 m each, were marked out and all larvae of *H. armigera* removed from the marked plots prior to treatment application. *Heliothis* NPV at 250 l/ha was sprayed alone, with Tinopal at 0.01%, and egg albumen at 0.3% + Tinopal at 0.01%, during evening hours using a knapsack sprayer at 500 l/ha. Three plots were randomly sprayed with each treatment, and 50 laboratory-reared, third-instar larvae were released on marked plants of the two middle rows of treated plots at 0, 24, and 48 h after treatment application. Care was taken to release not more than two to three larvae on individual sunflower heads. The larvae were allowed to feed *ad libium* for 24 h, then returned to the laboratory and reared individually on sunflower leaves until death or pupation. Observations on larval mortality were recorded daily. Virus persistence was expressed as the percentage of original activity remaining (OAR)<sup>8</sup> at various sample intervals.

### III. RESULTS AND DISCUSSION

#### A. Laboratory Studies

In both experiments, mortality in the untreated control was not observed, indicating that the laboratory cultures were free of virus infection. The additives significantly increased the mortality of both *H. armigera* and *S. obliqua* larvae due to their respective NPVs (Table 1). The highest mortality, 85.0% for *H. armigera* and 70.0% for *S. obliqua*, was recorded when egg albumen at 0.3% + Tinopal at 0.01% + soybean flour at 5% + jaggery at 5% were used as additives along with NPVs. This treatment was at par with other treatments, viz., cottonseed meal at 5%, soybean flour at 5 and 10%, egg albumen at 0.3% + Tinopal at 0.01% with or without jaggery at 5% or soybean flour at 5% in the case of *H. armigera*

TABLE 2  
Efficacy of *Heliothis* NPV Against *H. Armigera* on Pigeonpea and Chickpea as Influenced by Different Additives

Treatment*	Pigeonpea				Chickpea			
	Av % mortality	LT <sub>50</sub>	Pod damage (%)	Yield (kg/ha)	Av % mortality	LT <sub>50</sub>	Pod damage (%)	Yield (kg/ha)
Teepol (0.05%)	93.2	127.8	9.7 a-c	2003 a	79.2	229.3	10.6 bc	1726 b
Egg albumen (0.25%) + Tinopal (0.01%)	91.7	162.0	10.3 bc	1838 a-c	75.8	245.3	7.6 ab	1651 b
Egg albumen (0.05%) + Tinopal (0.01%)	95.00	151.8	8.8 a-c	2003 a	80.8	224.0	10.9 bc	1786 ab
Soybean flour (0.5%) + Teepol (0.05%)	98.3	140.4	10.5 bc	1687 c	79.2	245.2	11.2 c	1666 b
Cotton seed meal (0.05%) + Teepol (0.05%)	98.3	149.9	7.7 ab	2016 a	81.5	248.0	9.6 a-c	1696 b
Activated charcoal (0.1%)	90.0	159.0	7.5 ab	1879 ab	85.8	237.7	8.8 a-c	1741 b
Milk powder (0.1%)	96.7	132.1	6.5 a	1989 a	86.7	212.5	7.7 a-c	1726 b
Sodium lauryl sulfate (0.05%)	96.7	137.0	9.3 a-c	1756 bc	79.2	225.0	6.8 a	1905 a
Endosulfan (0.07%)	—	—	12.5 c	1962 a	—	—	7.5 ab	1696 b
Control	—	—	17.6 d	1687 c	—	—	15.3 d	1161 c
SEM			1.14	74.06			0.98	47.40

Note: Means followed by the same letter in a column are not significant different at  $p = 0.05$ .

\* NPV at 250 l/ha was used with different additives.

NPV. A similar trend was also observed with *S. obliqua* NPV. However, soybean flour at 5% was least effective in increasing the mortality of *S. obliqua*.

Cottonseed meal increased the mortality by 5 to 10%, soybean flour by 10 to 15%, and egg albumen at 0.3% + Tinopal at 0.01% by 20% in the case of *H. armigera*; the corresponding increases for *S. obliqua* were 20 to 25, 13 to 20, and 27%, respectively. Addition of jaggery or cottonseed meal to egg albumen + Tinopal did not increase mortality. However, addition of soybean flour at 5% marginally improved mortality in both cases. A reduction in LT<sub>50</sub> values from 4 to 30 h was observed for *H. armigera* due to incorporation of different additives. A similar comparison for *S. obliqua* was not possible, as the mortality with virus alone was less than 50%.

## B. FIELD STUDIES

### 1. Pigeonpea and Chickpea

#### a. Larval Mortality and LT<sub>50</sub> Values

Cumulative average percent mortality and LT<sub>50</sub> values (Table 2) revealed no appreciable differences in the percent mortality of *H. armigera* by incorporation of different additives. The average LT<sub>50</sub> values ranged from 127.8 to 162 h, respectively, in NPV sprayed at 250 l/ha with Teepol at 0.05% and egg albumen at 0.25% + Tinopal at 0.01%. However, there were no significant differences in LT<sub>50</sub> values when using different additives.

The cumulative percent mortality in chickpea ranged from 75.0% in NPV at 250 l/ha with egg albumen at 0.25% + Tinopal at 0.01% to 86.7% in virus + milk powder at 0.1%. Mortality differences using the different additives were not statistically significant.

### b. Percent Pod Damage

In pigeonpea, the use of milk powder at 0.1%, activated charcoal at 0.1%, and cottonseed meal at 0.5% + Teepol at 0.05% were equally effective and significantly superior to endosulfan at 0.07% and the rest of the additives in reducing pod damage. In chickpea, the use of sodium lauryl sulfate at 0.05% was a most effective treatment, but was no better than endosulfan at 0.07%. The rest of the additives, though significantly superior to the untreated control, were only as effective as endosulfan, except soybean flour at 0.5% + Teepol at 0.05%, which recorded significantly more damage than endosulfan.

Thus, additives such as milk powder at 0.1%, activated charcoal at 0.1%, cottonseed meal at 0.5% + Teepol at 0.05%, and sodium lauryl sulfate at 0.05% were effective in reducing pod damage in pigeonpea and chickpea.

### c. Yield

Additives such as milk powder at 0.1%, cottonseed meal at 0.5% + Teepol at 0.05%, and activated charcoal at 0.1%, which recorded significantly lower pod damage in pigeonpea also recorded higher grain yields, but were no better than endosulfan at 0.07%. The other additives, except soybean flour at 0.5% + Teepol at 0.05% and sodium lauryl sulfate at 0.05%, were on par with the above treatments. In chickpea, the highest yield of 1905 kg/ha was recorded from plots treated with virus + sodium lauryl sulfate at 0.05%. This treatment also recorded significantly lower damage. The remainder of the additives and endosulfan at 0.07% were about the same. (Table 2).

## 2. Sunflower

On sunflower, the addition of egg albumen and Tinopal increased the percent of mortality compared to virus alone or virus + Tinopal (Table 3). It was also observed that the persistence of NPV decreased in time with all treatments. However, the OAR values for virus + egg albumen + Tinopal were always higher than virus alone or virus + Tinopal.

Egg albumen primarily has value as a strong adhesive with some UV screening capacity.<sup>9</sup> Skimmed milk used as a UV screen has also been shown to have some wetting properties.<sup>7</sup> Sugarcane jaggery at 0.5%, cottonseed kernal flour at 1%, groundnut oil cake at 3%, and chickpea flour at 1% significantly increased the mortality of second-instar *H. armigera* larvae in pot culture studies. A combination of jaggery at 0.25%, chickpea flour at 0.25%, groundnut oil cake at 0.5%, and cottonseed oil cake at 0.1% improved the efficacy of the virus.<sup>16</sup>

The present findings indicated that the efficacy of the virus can be increased by the addition of one or more adjuvants. Jaggery, soybean flour, and cottonseed meal could have acted as phagostimulants, enabling the larvae to acquire more virus and thereby causing higher mortality. Tinopal, egg albumen, and sodium lauryl sulfate may be useful as sunlight-reflectant, sticker/absorbant, wetting: dispersing agents, respectively.

## IV. SUMMARY

Laboratory and field studies were conducted to evaluate different adjuvants with a view to improving the effectiveness of nuclear polyhedrosis viruses of *Heliothis armigera* and *Spilosoma obliqua*. Laboratory studies revealed that egg albumen at 0.3% + Tinopal at 0.01% increased the mortality of *H. armigera* and *S. obliqua* by 20 to 25%. Addition of jaggery or cotton seed meal to egg albumen + Tinopal did not increase the mortality. Field studies conducted to evaluate different adjuvants for increased effectiveness of *Heliothis* NPV against *H. armigera* on pigeonpea and chickpea revealed that the addition of Teepol, egg albumen + Tinopal, activated charcoal, milk powder, and sodium lauryl sulfate resulted in less pod damage and increased yield.

### TABLE 3

Treatment	Hours after treatment								
	24			48			72		
	No. larvae	Mortality (%)	OAR	No. larvae	Mortality (%)	OAR	No. larvae	Mortality (%)	OAR
NPV 250 l/ha	35	74.3	100	40	62.5	70.67	37	48.6	65.5
NPV + 250 l/ha + Tinopal (0.01%)	36	77.8	100	32	62.5	80.4	34	53.0	68.1
NPV 250 l/ha + egg albumen (0.3%) + Tinopal (0.01%)	34	91.2	100	38	81.6	89.5	34	61.8	67.8



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## *Appendix*

Formulations and Applications of Adjuvants for Agrichemicals: A Selected  
Bibliography of World Literature in English

## APPENDIX

**FORMULATIONS AND APPLICATIONS OF ADJUVANTS FOR  
AGRICHEMICALS: A SELECTED BIBLIOGRAPHY OF WORLD  
LITERATURE IN ENGLISH (REVISED AND UPDATED)****PREFACE**

The second edition of the Adjuvants Bibliography of Literature until 1986 appeared in the Proceedings of Adjuvants and Agrochemicals, Volume 2 published by CRC Press in March 1989. Since 1986, research has continued and numerous papers have been published on adjuvant use in formulations and applications. Therefore, the Organizing Committees of the First and Second Adjuvants Symposium initiated a joint project to search the world English literature on adjuvants and update the bibliography once again.

*Adjuvant* is a general word which may refer to any of the following terms, many of which are used interchangeably: activators, additives, antidotes, antidrift agents, antifoam agents, chelates, dispersing agents, conditioners, emulsifiers, enhancing agents, extenders, inorganic salts, modifiers, oils, penetrants, protectants, safeners, stickers, spreaders, surface-active agents, surfactants, water (rain) or insect repellants, wetters, and wetting agents.

Adjuvants are important ingredients of agrichemical products such as herbicides, insecticides, fungicides, nematicides, desiccants, defoliants, plant growth regulators, fertilizers and soil conditioners, or amendments.

Adjuvants are also used in foods, pharmaceutical drugs, cleaners, detergents, beauty aids, and shampoos as well as for industrial purposes in gasolines, cement plasticizers, rock-fracturing agents (for drilling oil wells and reservoirs), and dust inhibitors (in coal mining). The numerous terms describing adjuvants make searching the literature difficult. Although the Committees have made an extensive manual search in agricultural scientific journals, technical reports, and a computer-assisted survey of *Agricola*, the search methods used are by no means exhaustive. Therefore, some titles may have been excluded.

Journal titles are abbreviated as set out in the guide, *Series Sources for the BIOSIS Data Base* (Volume 188, published by BIOSIS, Philadelphia). Alphabetization of the list itself was done according to AACR2 filing rules. The committees would like to express their appreciation to the reference services of the libraries of Agriculture Canada (Ottawa and Brandon), University of Manitoba (Winnipeg), and Virginia Polytechnic Institute and State University (Blacksburg, VA) for their assistance in completing and verifying references, and to Carol Enns, Desiree Czerkawski, Brenda Eamer, and Carol Vallance for their work on the bibliography.

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